Measuring anaerobic sludge digestion and growth by a simple alkalimetric titration

S. R. Jenkins, J. M. Morgan, C. L. Sawyer

Anaerobic digestion, although widely used as a wastewater sludge treatment process, continues to be a process that is very difficult to maintain at high efficiency. Organic acids produced in the process tend continuously to depress pH below a point where the acids can be converted to methane. As a result, a large buffering capacity is required to maintain the pH between 6.7 and 7.4, which allows efficient operation. Present tests to measure this buffer capacity are inadequate. Total alkalinity and bicarbonate alkalinity measurements, as normally carried out by plant operators, produce invalid results in the presence of large quantities of organic acids. Failure to distinguish between this measured alkalinity and the true bicarbonate alkalinity (TBA) may result in sudden digester failure.

To date, attempts to determine TBA and correlate these test results to digester performance have generally proven inadequate. O'Brien *et al.*[1] and Barber[2] have used both total alkalinity and volatile acid measurements to estimate TBA. Both of these methods, as well as the volatile acid test alone, employ cumbersome laboratory techniques and have not been shown to adequately predict impending digester problems.

The present research proposes a simple but adequate test that will provide plant operators with accurate information on anaerobic digester efficiency, as well as considerable long-range insight into digester operation. Because the entire operating efficiency of many wastewater treatment plants is determined by the success of the anaerobic digesters, the predictive capability of the proposed test would not only eliminate many operational headaches, but would also allow for more efficient treatment plant operation, thus resulting in higher quality effluent per unit cost.

The anaerobic system is a two-stage symbiotic biochemical process consisting of acid fermentation and methane fermentation. In acid fermentation, complex organics are hydrolyzed by "acid-forming" bacteria that produced short-chain (volatile) acids. These acids are then converted to methane in the second stage, which is controlled by the strictly anaerobic "methane-forming" bacteria. Methane bacteria are slow growers, making them the rate-limiting factors. Methane bacteria are also very sensitive to pH, requiring a pH between 6.7 and 7.4. In this pH range the bicarbonate system greatly influences, and in most cases controls, the buffering capacity of the sludge. As shown by Stumm and Morgan,[3] the bicarbonate ion provides buffer capacity over an approximate range of pH from 5.3 to 7.3. On the other hand, the volatile acids formed in the anaerobic process offer little buffering in this pH range. The two major organic acids formed, acetic and propionic, offer significant buffer capacities only in the pH range close to their pk values, 3.7 to 5.7, and 3.9 to 5.9, respectively.[4]

The buffer capacity of most wastes and waste sludges is determined using an alkalinity titration. Alkalinity is defined as the acid neutralizing capacity of a solution to a specified endpoint. Unfortunately, when considering anaerobic digesters, most currently accepted alkalinity results include not only the utilizable bicarbonate buffering capacity, but also the useless buffering intensity of the organic acids. In an effort to provide a number more representative of the true buffer intensity of the sludge, several tests are currently accepted or proposed. These tests are inadequate, as pointed out below. These methods calculate what is referred to as the true bicarbonate alkalinity (TBA). The term TBA, itself, may be a misnomer, as a sludge may contain such compounds as phosphates, which also contribute to the alkalinity in the pH range of interest.

The proposed procedure more adequately describes the buffering capacity of digester systems and thus is a measure of their efficiency.

It may also be of interest to note that the endpoint for the alkalinity test, to include all of these buffering systems, has been arbitrarily set at pH 4.3. Although possibly chosen to allow utilization of the familiar colorimetric indicator (such as methyl orange) for this endpoint, no theoretical justification for this endpoint pH exists. If the system in question was pure water containing only 10^{-3} M (50 mg/L as $CaCO_3$) carbonate compounds, the alkalinity endpoint would be properly chosen at pH 4.3. For such a water, the endpoint is as sharp as the slope of the titration curve is steep at this pH. For natural river waters as discussed recently by Pearson,[5] this endpoint can no longer be justified. The anaerobic sludge system is even farther from a pure water system, and the bicarbonate concentration normally varies between 0.04 to 0.1 moles/L (2 000 to 5 000 mg/L as $CaCO_3$). The titration endpoint for the sludge is not sharp at pH 4.3, thus offering no advantage. Because of the variability of anaerobic sludges, no theoretically exact endpoint could be proposed. However, one superior to a pH of 4.3 may be offered.

EXISTING METHODS

The current methods for calculating TBA require determination of total alkalinity to pH 4.3 ($ALK_{4.3}$) and the volatile acids (VA), which are mostly acetic and propionic acids. The TBA based on an alkalinity endpoint of 4.3 ($TBA_{4.3}$) is calculated using the following equation:

$$TBA_{4.3} = ALK_{4.3} - 0.85 \times VA \qquad (1)$$

Use of this equation assumes that 85% of the volatile acids have been titrated at pH 4.3.

The $ALK_{4.3}$ is determined by titration. The VA are determined by one of three methods outlined in "Standard Methods."[6] Each of these volatile acids methods has inherent problems.

The steam-distillation method involves filtering the sludge and distilling the filtrate to determine the volatile acid concentration. Although 95% volatile acids is recovered in this method, elaborate distillation equipment is required. The steam-distillation method is also very time consuming, taking 4 hours to complete.

The straight-distillation method is a simpler modification of the above and is the method of choice for many plant operators. It is an empirical method that involves acidifying the centrifuged supernatant and distilling it for 1 minute per 5 mL. After distillation, the sample is titrated to the phenolphthalein endpoint (pH = 8.3). This method has variable recovery and only distills about 70% of the volatile acids present. Reproducible results are somewhat difficult, and the test requires over an hour.

The final method for VA discussed in "Standard Methods" is a chromatographic-separation method. This method involves acidifying a centrifuged supernatant and adsorbing it in a column of silicic acid. The organic acids are eluted with n-butanol in chloroform. The eluted sample is titrated with a standard base to find the amount of volatile acid present. This method has about 95% recovery of the volatile acids. The silicic acid used is difficult to work with. It must be a mesh size of 50 to 200 and completely dry. Also, a nitrogen atmosphere must be maintained while titrating. This test also requires considerable time.

Regardless of which of these three volatile acids tests is used, the VA value obtained is subtracted from the $ALK_{4.3}$ to obtain $TBA_{4.3}$. The subtraction compounds the significant errors in the two tests, resulting in unreliable $TBA_{4.3}$ data. Occasionally, even completely erroneous negative numbers result.

O'Brien *et al.*[1] has proposed a direct-titration method to determine TBA. This method, which is not in "Standard Methods," involves titrating a centrifuged supernatant to a pH of 3.3, recording this as total alkalinity$_{4.3}$, then boiling the sample to remove CO_2. The sample is titrated to a pH of 4.0, then 5.3. The value between 4.0 and 5.3 gives the volatile-acid concentration. In order to account for only 83% of the volatile acids being titrated to the total alkalinity endpoint, the VA value obtained is multiplied by a factor of .83. Some controversy exists about the accuracy of this multiplier.[2] The resulting equation is then:

$$TBA = ALK_{4.3} - 0.83 \times VA \qquad (2)$$

The back titration and boiling required in this test are cumbersome.

In summary, none of the existing methods for determining alkalinity are simple, nor do they adequately describe the buffering system in an anaerobic digester. For these reasons, an alternative method was proposed and validated.

PROPOSAL

It was proposed to introduce a new alkalinity titration with an endpoint of pH 5.75, instead of the normal pH 4.3. As discussed above, the endpoint of pH 4.3 for alkalinity titrations of sludges is arbitrary. Consequently, it seems inappropriate to select an endpoint that requires titration of compounds that offer no usable buffer capacity in the system in question and that, in fact, must be subtracted to get usable results. On the other hand, if the endpoint of the alkalinity determination is pH 5.75, the useful buffer capacity of the bicarbonate system is measured, but the unusable volatile acids buffering capacity is not.

At pH 5.75, 80% of the bicarbonate will have been titrated, as determined from a distribution diagram or from equilibrium equations. As discussed by Stumm and Morgan,[3] approximately 80% of the bicarbonate ion present in a water will be converted to carbon dioxide when the pH is lowered to pH 5.75 during titration with acid. Similarly at this pH, less than 20% of the volatile acids will have contributed to the alkalinity. Consequently, even if the total volatile acids reach a concentration of 500 mg/L as $CaCO_3$, and the TBA is 2 000 mg/L, less than 5% error is introduced by not subtracting them from a titration to pH 5.75 result. Thus realistically, unlike the established methods, the measured alkalinity to pH 5.75 ($ALK_{5.75}$) gives a direct measure of the usable buffer capacity of a digester. For comparison's sake, the true bicarbonate alkalinity using the pH 5.75 endpoint ($TBA_{5.75}$) can be calculated using the equation:

$$TBA_{5.75} = 1.25 \times ALK_{5.75} \quad (3)$$

EXPERIMENT

Field studies. Regionally available sludges were used to affirm the reliability of the proposed titration for accurately determining TBA and describing the digestion condition of sludges.

Sludges from nine area waste treatment plants were obtained and the $ALK_{4.3}$, $ALK_{5.75}$, and volatile acids were determined using techniques outlined in "Standard Methods."[6] The volatile acids were determined using the silicic-acid technique discussed above. Where available, both primary and secondary digesters were sampled. A total of 16 sludges were analyzed. Each sample was gathered and preserved at 4°C. All tests were run after the samples were brought back to the lab and within 24 hours of the collection. The sites were all municipal wastewater treatment facilities, including plants in Montgomery, Prattville, Sylacauga, Anniston, Phenix City, and Auburn. The plants were all of the trickling-filter type, except for Anniston, which was activated sludge. The Auburn Northside Plant, Prattville Plant, and especially the Sylacauga Plant, appeared to be overloaded. Strong pungent odors were observed at these plants. Tests were performed on the sludges, as well as on centrifuged supernatants of the sludges. Results of the supernatant TBAs, and of the sludges themselves, are shown in Table 1. Calculated values of $TBA_{5.75}$ as determined by the method proposed herein compared favorably to $TBA_{4.3}$ values calculated using Equation 1.

As may be seen, the $TBA_{5.75}$ determined using the proposed titration compared very well with values obtained by the conventional, $TBA_{4.3}$, method. The differences in most cases between the calculated TBAs for a given sludge or supernatant are less than 10%. The proposed method, which is analytically much simpler than the other method, adequately describes all ranges of digester activity. It accurately described activity ranging from the critical inactivity of the digesters at the Auburn Northside and Sylacauga plants to the very stable conditions of those at the Econchate and Anniston plants. Unlike the standard tests, completely erroneous test results, such as the negative 2 549 mg/L shown for the Sylacauga plant, never result. The proposed test is also superior to currently accepted tests in more accurately detecting the usable buffer capacity for very stable sludge, like those found in the Anniston plant and Auburn Southside plant. For these plants, the VA was extremely low. The $ALK_{4.3}$ was extremely high, yet 60 to 75% of the buffering capacity was determined to be below pH 5.75. This buffering is of no use in a digester and should not be referred to as "bicarbonate alkalinity." The proposed titration gives a much more realistic picture of the usable buffer capacity of the sludges from these two plants.

Table 1—True bicarbonate alkalinity of municipal digester sludges. All alkalinities are mg/L as $CaCO_3$.

	Supernatant		Sludges	
Plant	$TBA_{4.3}$	$TBA_{5.75}$	$TBA_{4.3}$	$TBA_{5.75}$
Auburn				
Northside				
Primary	Negative	0	−332	0
Secondary	135	350	280	312
Southside	Not run	Not run	2 898	1 812
Montgomery				
Towassa				
Primary	1 650	1 600	2 382	1 812
Secondary	1 980	1 812	6 200	6 000
Econchate				
Primary	3 100	3 125	3 388	3 312
Secondary	3 250	3 562	4 842	4 125
Cotoma				
Primary	2 490	2 437	3 500	3 062
Secondary	3 185	3 250	4 916	5 625
Anniston				
Primary 1	2 434	2 000	7 392	2 750
Primary 2	2 195	1 750	8 184	2 750
Secondary	2 470	2 062	5 920	2 625
Prattville	665	800	846	687
Sylacauga	Negative	0	−2 549	0
Talladega				
Primary	2 033	1 812	2 177	1 937
Secondary	2 144	1 750	2 144	2 062

A least squares analysis comparing the TBAs for the two methods for the sludge supernatant samples is shown in Figure 1. An excellent correlation exists, resulting in a regression coefficient of 0.95. Because of the inability of the currently accepted test to adequately describe the TBA as discussed above, a similar least squares was not determined for the sludge samples.

Laboratory studies.

Shock-loaded digester. A single laboratory-scale anaerobic digester was set up in the manner suggested by Metcalf and Eddy[7] to ascertain the response of the proposed titration technique to changes in metabolic activity that may occur during anaerobic processes. The initial sludge was obtained from the digester at the Southside Plant in Auburn. The sludge was held in the

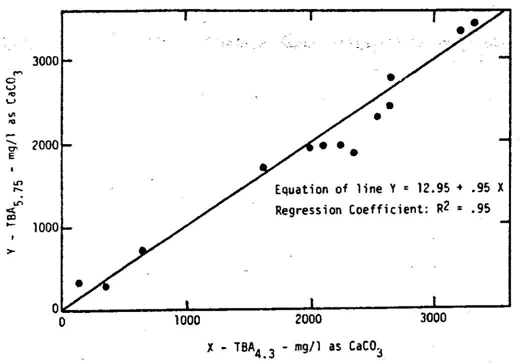

Figure 1—Least square regression analysis for TBAs titrated to pH 5.75 and pH 4.3 for the municipal digester sludges.

laboratory digester for a period of time to ensure that truly anaerobic conditions prevailed. It was then shock-loaded with a concentrated glucose solution. The digester was not fed again until a second (lesser) shock-load was applied 11 days later. The response of the digester to these shock-loadings is evidenced by the data reported in Figure 2. The initial shock-loading occurred at a time corresponding to day 0. The second such loading was applied on day 11.

Although both methods respond to the changing conditions related to the shock-loading, it is most important to note that the total bicarbonate alkalinity, as determined by the proposed method, was much more sensitive to changing conditions within the digester as measured by gas production. This is true in spite of the fact that the proposed method is much simpler and is, therefore, more likely to be used correctly by plant operators.

Continuous-flow digesters. To evaluate the proposed test as it relates to normal wastewater plant digester operation, four digesters, similar to the one described above, were set up and fed daily with primary sludge taken from the Auburn Southside Plant. The digesters were operated for approximately 1 month (one theoretical detention time), and were then subjected to various organic loadings. The operating efficiency of each

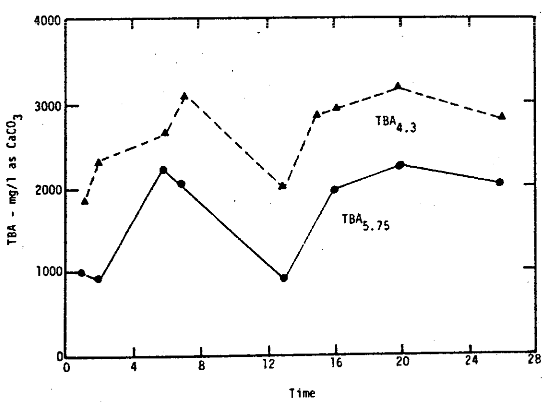

Figure 2—The true bicarbonate alkalinity (TBAs) by titration to pH 4.3 and 5.75 versus time for a laboratory-scale anaerobic digester shock-loaded with a concentrated glucose solution.

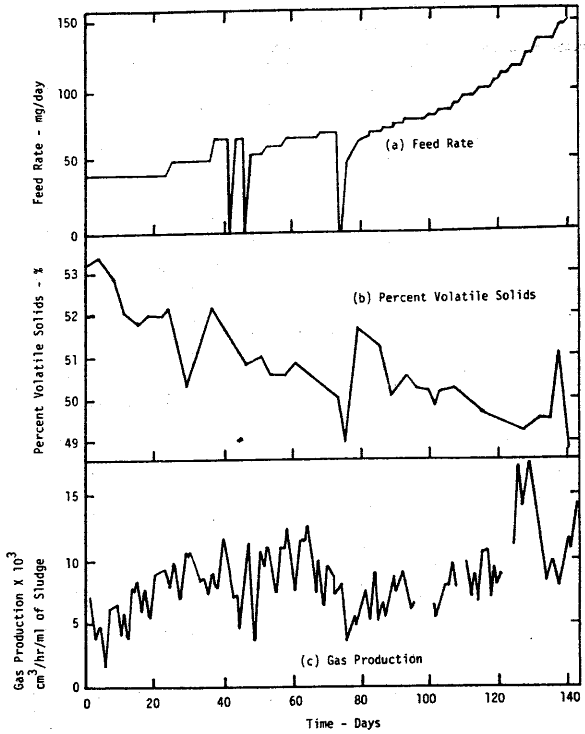

Figure 3—Feed rate (a), percent volatile solids (b), and gas production (c) versus time for a laboratory-scale anaerobic digestion feed daily with municipal primary sludge.

digester was closely monitored as a function of time and feed rate by measuring gas production, volatile solids reduction, volatile acids, total alkalinity, and $TBA_{5.75}$. Results typical of all digesters are shown in Figure 3.

During digestion, gas production is considered indicative of the stabilization of the waste in the digester. The total gas produced was easily measured, and it provided an indication of digester activity. A graph of the gas production is included in Figure 3c. An increase in feed rate produces a rise in gas production unless the feed rate is too high; then production of gas goes down because of excess acid production. This rise in gas production can be seen on day 113, when the feed rate was increased from 95 to 100 mL/d. The following day, gas production jumped from 6.31×10^{-3} to 10.18×10^{-3} $cm^3/mL \cdot h$ of sludge in digester. After this sudden initial rise in gas production, the production level dropped again.

A comparison between the $TBA_{4.3}$ and $TBA_{5.75}$ for the sludge, as a function of time, is shown in Figure 4a. This figure shows that while $TBA_{4.3}$ is usually about 1 000 mg/L as $CaCO_3$, higher than $TBA_{5.75}$, the difference is pretty much a constant.

The two TBAs for the supernatant are essentially the same (Figure 4b). The only significant difference is that the proposed $TBA_{5.75}$ test indicates more daily variation than the $TBA_{4.3}$ standard test. It is believed that day-to-day variation in the digester was correctly monitored by $TBA_{5.75}$, while being missed by $TBA_{4.3}$.

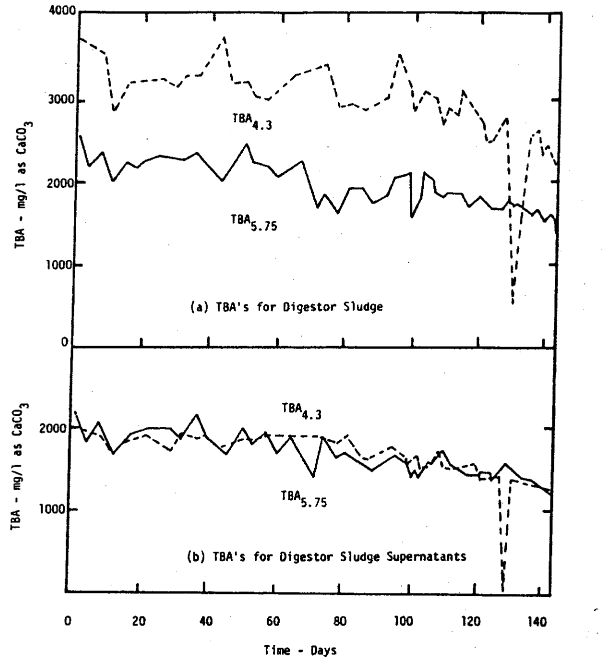

Figure 4—The TBAs by titration to pH 4.3 and pH 5.75 versus time for laboratory digester sludge (a) and supernatant (b) taken from a digester feed daily with municipal primary sludge.

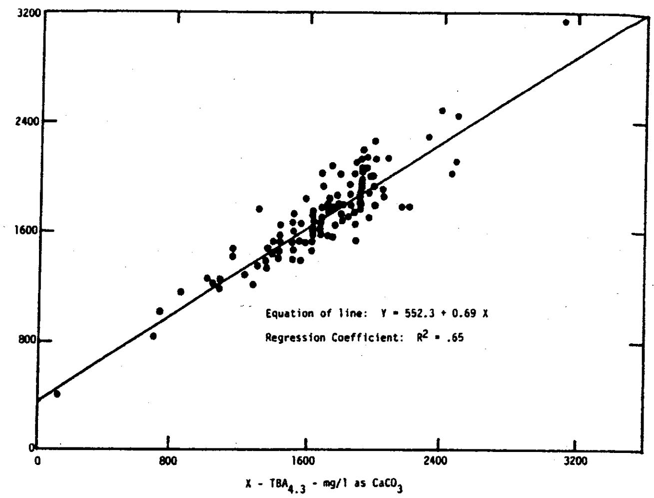

Figure 5—Least square regression analysis for TBAs titrated to pH 5.75 and pH 4.3 for the supernatant from all four laboratory digesters.

For example, the feed rate of the digester was gradually increased between Days 45 and 75 (Figure 3a). Although fluctuating considerably, the gas production increased and then steadily decreased through that period, indicating changing digester conditions (Figure 3c). As the gas production changes, there is a corresponding change in $TBA_{5.75}$, but relatively no change in $TBA_{4.3}$, again indicating that $TBA_{5.75}$ gives a better representation of the actual digester activity.

Only on Day 130 did $TBA_{4.3}$ change substantially when $TBA_{5.75}$ did not. Although the gas production did show a changing system, the sludge activity, shown by the gas production on either side of the spike, was only gradually changing. Thus, even at this date, the $TBA_{5.75}$ actually gave a more plausible indication of digester activity.

The other three digesters produced similar results. $TBA_{4.3}$ and $TBA_{5.75}$ of the sludge were approximately 1 000 mg/L as $CaCO_3$ apart, but the supernatant true bicarbonate alkalinities were very similar. Again, $TBA_{5.75}$ was more sensitive to changes in feed rate than was $TBA_{4.3}$. Even when one digester failed, $TBA_{5.75}$ correctly detected approaching stress and ultimate failure.

A least squares analysis comparing $TBA_{4.3}$ and $TBA_{5.75}$ for the supernatant of all the digesters is shown in Figure 5. The regression coefficient of 0.65 indicates a correlation between the two methods. Once again, because of the standard test's inability to accurately detect the useful buffer capacities of the sludges when the VA is low, the regression coefficient comparing $TBA_{4.3}$ and $TBA_{5.75}$ for the sludges is lower, and not shown.

The only possible advantage the standard alkalinity test may have over the proposed test is that the slope of the titration curve may be steeper at pH 4.3 than at pH 5.75. That is, the endpoint could be more easily identified. For many sludges, this is not true, as shown in Figures 6, 7, and 8. When a standardized pH meter is used and read to a precision of ±0.05 pH units for both tests, equally accurate endpoints result. In both cases, the samples should be titrated slightly past the endpoint, as outlined in "Standard Methods."[6] The amount of acid required to bring the sample to the required endpoint is then more accurately taken off the titration curve. If the preselected pH titration method

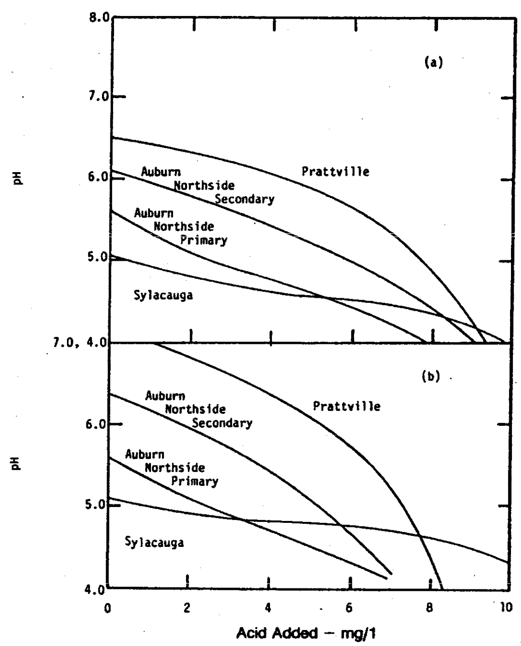

Figure 6—Titration curves for (a) sludges and (b) sludge supernatants from critically inactive municipal digesters.

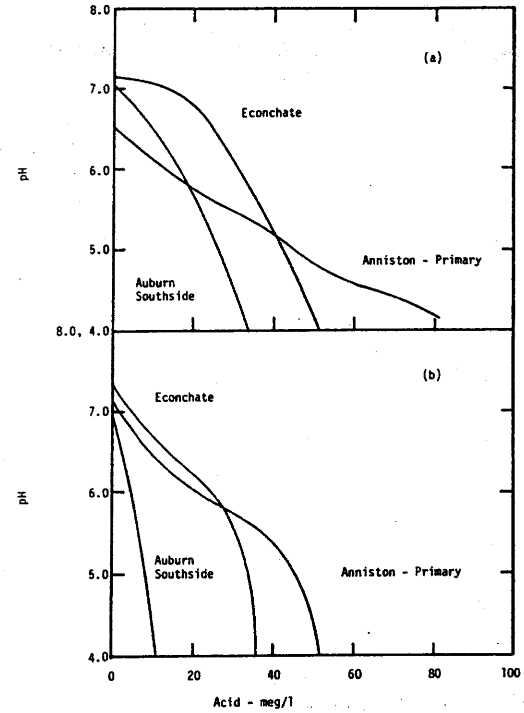

Figure 7—Titration curves for (a) sludges and (b) sludge supernatants from stable municipal digesters.

is used, a standardized pH meter gives more than adequate precision for either endpoint 4.3 (which implies 4.30) or 5.75.

The titration curves shown in Figure 6 are for both municipal sludges and supernatants of digesters critically inactive and containing high volatile acids (Auburn

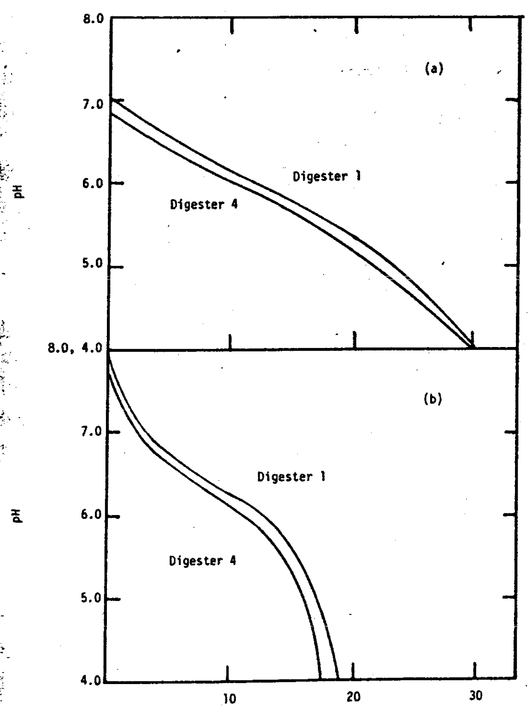

Figure 8—Titration curves for (a) sludges and (b) sludge supernatants from laboratory digesters.

Northside, Prattville, and Sylacauga). It can be seen that the endpoints at pH 5.75 and pH 4.3 are equally sharp. Even when the very stable sludges of Auburn Southside and Anniston are considered (Figure 7), only the pH 4.3 endpoints for the supernatants are significantly sharper. Similar results were obtained for the sludges and supernatants from the digesters (Figure 8).

Thus, the titration to pH 4.3 would have a slight advantage only for sludge supernatants. However, as seen in Figure 2 and Figure 5, both methods correlate well for the supernatants when a standardized pH meter is used for the titration. The simplicity of the proposed titration method far outweighs any slight advantage the presently accepted titration procedure might have. More reliable results for TBA are obtained using the proposed titration to pH 5.75.

SUMMARY

In summary, it would seem that an alkalimetric titration to pH 5.75 can be used routinely to monitor laboratory and actual anaerobic digester performance with a high degree of confidence. The simplicity of the test should encourage many operators to pay more attention to digester performance and, therefore, result in improved wastewater treatment efficiency.

ACKNOWLEDGMENTS

Credits. This research was supported in part by the Auburn University Engineering Experiment Station.

Authors. Stephen R. Jenkins is an associate professor, Department of Civil Engineering, Auburn University, Ala. Joe M. Morgan is an associate professor, Department of Civil Engineering, Auburn University, Ala. Cynthia L. Sawyer is an engineer, Container Corporation of America, Fernandina Beach, Fla. Correspondence should be sent to Stephen R. Jenkins, Department of Civil Engineering, Auburn University, AL 36849.

REFERENCES

1. O'Brien, J. E., and Donlan, R. J. "Direct Method for Differentiating Bicarbonate and Acetate in Digester Contol." Presented Div. of Enviro. Chem., ACS, New Orleans (March 1977).
2. Barber, N. R., "Keep Your Digester in Good Shape." *Water and Wastewater Engineering,* **14,** 9 (1978).
3. Stumm, W., and Morgan, J. J., *Aquatic Chemistry,* Wiley Interscience, 176 (1981).
4. "Advantages of Sodium Bicarbonate in Water and Wastewater Treatment." Brochure, Church & Dwight (1978).
5. Pearson, R., "Fixed endpoint alkalinity determination." *J. Water Pollut. Control Fed.,* **53,** (July 1981).
6. *Standard Methods for the Examination of Water and Wastewater.* 15th Edition, American Public Health Association (1978).
7. Metcalf and Eddy, Inc., *Wastewater Engineering: Collection, Treatment Disposal.* McGraw-Hill Book Co., New York, N.Y. (1972).