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ANAEROBIC PROCESS CONTROL BY INORGANIC CARBON ANALYSIS

1. INTRODUCTION

Stability in the anaerobic treatment of sludges and of industrial wastewaters is closely related to the uffering action of CO_2/HCO_3^- and to the total volatile acids concentration (TVA) and requires the monioring of the following parameters: H^+, TVA, total alkalinity (TA) and bicarbonate (HCO_3^-) concentrations n the digester mixed liquor and CO_2/CH_4^- ratio in the gas [1, 4-7].

Routine process analysis is based on TA and TVA titrations and HCO_3^- determination (eq. (1)). As vell known, TVA analysis [2] is time consuming and not very accurate.

In this note a simple procedure for the calculation of HCO_3^- alkalinity in digester mixed liquors, based on an inorganic carbon mass balance, is presented.

2. METHODS AND MATERIALS

Neglecting weak anions, such as phosphates and silicates, the alkalinity balance gives bicarbonate concentration in a water solution:

$$HCO_3^- = TA - 0.833 \cdot (1-a) \cdot TVA, \tag{1}$$

where:

HCO_3^- – bicarbonate concentration as $CaCo_3$;
TA – total alkalinity concentration as $CaCO_3$;
TVA – total volatile acids concentration as CH_3COOH;
0.833 – equivalent weights ratio $CaCO_3/CH_3COOH$;
a – fraction of ionized acid in solution at the final titration pH (for CH_3COOH and pH = 3.7, a = 0.08).

Bicarbonates can also be determined from an inorganic carbon (IC) balance in solution:

$$IC = CO_2 + HCO_3^- + CO_3^{=}. \tag{2}$$

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If pH $\leqslant 8$ (as in anaerobic digesters) then $CO_3^{=}$ is negligible:

$$CO_3^{=} \leqslant 6 \cdot 10^{-3} \cdot IC \quad (T = 37°C)$$

and eq. (2) is reduced to:

$$HCO_3^- = IC - CO_2.$$

The following quick and easy method for determining the HCO_3^- concentration in digester mi liquors has been adopted:

1. Calculation of concentration of CO_2 in mixed liquor as a function of partial pressure of CO_2 gas, according to Henry law (assuming equilibrium conditions at the gas/liquid interfaces).
2. Determination of inorganic carbon concentration in the mixed liquor.
3. Determination of TA by strong acid/weak base titration.
4. Calculation of HCO_3^- concentration by eq. (4) and of TVA concentration by eq. (1).

The method was tested on mixed liquor and gas samples from laboratory and pilot plant (5 dm^3 a 2 m^3, respectively) digesters fed with olive oil mill wastewaters (TOC = 15,000 to 30,000 mg/dm^3; CO = 35,000 to 70,000 mg O_2/dm^3; K = 3,000 to 6,000 mg/dm^3).

Concentrations of gaseous CO_2 were determined by injecting gas samples into the inorganic chan of a Beckman, Fullertion, Mod. 915 Total Organic Carbon Analyser, using pure CO_2 as reference [

Concentration of CO_2 in mixed liquor was calculated assuming Henry constant $H_{37°C} = 2211$ b mole/mole.

Inorganic carbon concentration in mixed liquor was determined by using the same TOC analys Because of the significance of IC determinations, stripping of CO_2 from the samples was carefully avoide

Total alkalinity was determined by potentiometric titration using 0.02N H_2SO_4 in a radiomete Copenhagen, ABU 12 Autoburette.

3. RESULTS AND DISCUSSION

Concentrations of HCO_3^-, determined by the proposed IC method (BA_1) and by traditional TA/TV procedure (BA_2), are for comparative reasons given in the table. The values obtained by the IC metho are always lower than those obtained by TA/TVA method (7÷14% 7); these differences are explaine in the following way:

IC errors: BA_1 values are affected by errors in IC and CO_2 determinations. IC instrumental erro on 915 TOC Analyser are of order of 1%; errors due to a lack of balance between liquid/gas interface and/or those due to evaluation of Henry constant are difficult to estimate; nevertheless the influence shoul be weak (≈ 1.5%), as in ordinary digester conditions $CO_2 \leqslant 0.15 \cdot IC$, and a 10% error in determinatio of $[CO_{\%}]$ does not seem possible; hence reliable HCO_3^- measurements can be obtained by the IC metho and the accuracy depends mainly on the instrumentation performance.

TA/TVA errors: BA_2 values are considerably affected by the following analytical errors: 1. TA titra tion takes also account of the contribution of the weak anions such as phosphates, silicates etc.; 2. TV chromatographic analysis does not allow a complete extraction of the organic acids (recovery $\geqslant 95\%$ Consequently, BA_2 values determined by TA/TVA procedure are surely overestimated.

TVA determination making use of HCO_3^- (by IC method and TA titration) is not accurate (overest mated values are obtained) because alkalinity related to PO_4^- etc. (which in the traditional method affect the HCO_3^- value) is now "transferred" completely on TVA (eq. (1)).

In order to obtain more reliable TVA values by the IC method, a correction factor ΔTA excludin the influence of the interfering weak anions can be calculated as follows:

$$\Delta TA = TA - BA_1 - TVA, \qquad (5$$

where TVA is determined by an independent method on few samples only.

Table

HCO_3^- determinations by TVA/TA and by proposed IC methods
Oznaczenie HCO_3^- za pomocą metody TVA/TA oraz proponowanej metody IC

IC mg/dm³ C	CO_2 (gas) %	CO_2 (sol.) mg/dm³ C	$(HCO_3^-)_1$ mg/dm³ $CaCO_3$	TA mg/dm³ $CaCO_3$	TVA mg/dm³ HAc	pH	$(HCO_3^-)_2$ mg/dm³ $CaCO_3$	$\frac{\Delta(HCO_3^-)}{(HCO_3^-)_2}$ %
898	39.8	117	3252	4270	849	7.07	3620	10.2
805	39.0	115	2875	3937	765	7.00	3351	14.2
173	25.8	76	402	925	610	6.39	468	14.1
790	35.0	103	2863	4440	1758	7.05	3093	7.4
900	36.0	106	3308	4700	1289	7.06	3712	10.9
1120	42.0	124	4150	6820	3000	7.05	4521	8.2

CO_2 Henry constant $H_{37°C}$ = 2211 bar

The above procedure implies constant concentration of interfering weak anions, which is a reasonable assumption for digester in steady-state operation. This correction is not really necessary because, in anaerobic process monitoring, the variations of control parameters are more important than the absolute values.

In conclusion, the inorganic carbon procedure for determining HCO_3^- concentration is a quick and reliable method for anaerobic process monitoring which could easily be automated by TA and IC (mixed liquor and gas) instrumental analyses.

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