

Determination of FOS/TAC Value in Biogas Reactors

DOC316.52.93087

Based on the Nordmann method

1. Introduction

The FOS/TAC ratio is an indicator for assessing fermentation processes. The TAC value is an estimation of the buffer capacity of the sample and the FOS value corresponds to the volatile fatty acids content. It is calculated empirically according to the Nordmann method.

2. Principle

A sample of 5 mL of fermentation substrate is titrated by 0.1 N of sulfuric acid solution (H_2SO_4) up to pH 5.0 to calculate the TAC value, expressed in mg/L of calcium carbonate ($CaCO_3$). Then the FOS value is obtained after a second titration step between pH 5.0 and pH 4.4. It is expressed in mg/L of acetic acid (CH_3COOH).

The Nordmann method for FOS determination is based on experiments with 20 mL of sample and 0.1 N H_2SO_4 of solution. The formula is adapted with a 5 mL sample. It is important to perform the titrations as close as possible to these conditions.

3. Electrode and reagents

Electrode: Combined pH electrode with temperature sensor, IntelliCAL PHC805

pH buffers: See [9.1 Electrode calibration on page 4](#)

Titrant: Sulfuric acid, H_2SO_4 0.1 eq/L solution in deionized water

Deionized water

4. Settings

4.1. FOS/TAC determination

The settings have been defined with:

- Sample volume: 5 mL (weighed as 5 g)
- Titrant concentration: 0.1 eq/L (corresponding to a 0.05 mol/L H_2SO_4 solution)
- Syringe volume: 10 mL

Name	Default parameter	Unit
Application		
Application name	FOS-TAC value	
Advisable syringe	10 mL	
Sample		
Name	Sample ? ¹	
Amount	5.00	[mL]
QC		
Name	QC Sample	
Electrode		
Recommended	PHC805	
Titrant H_2SO_4 0.1N		
Name	H_2SO_4	
Real concentration	0.1000	[eq/L]
Sample homogenization		
Active	No	
Time	15	[s]
Stirring speed	25	[%]
Message	Sample homogenization, please wait...	
pHi		
Active	No	

¹ "?" in the name, indicates that the sample name will be automatically incremented with a number for each analysis

Name	Default parameter	Unit
Max. stability time	120	[s]
Stability criterion	0.050	[pH/min]
Stirring speed	0	[%]
Result 1 (R1) name	pHi	
R1 hide	No	
R1 min.	0	[pH]
R1 max.	14	[pH]
R1 QC min.	0	[pH]
R1 QC max.	14	[pH]
FOS/TAC		
Active	Yes	
Stirring speed	25	[%]
Predose ordinate	6	[pH]
Predose speed	20	[mL/min]
Delay	10	[s]
Max. vol. stop point	25	[mL]
Ordinate stop point	4.0	[pH]
Stop on last EQP	Yes	
EP1 ordinate	5.0	[pH]
EP2 ordinate	4.4	[pH]
Result 1 (R1) name	TAC	
R1 hide	No	
R1 min	0	[mg/L]
R1 max	25000	[mg/L]
R1 QC min	0	[mg/L]
R1 QC max	25000	[mg/L]
R1 EQP index	1	
R1 molar weight	100.087	[g/mol]
Result 2 (R2) name	A	
R2 hide	Yes	
R2 min	0	[mL]
R2 max	25	[mL]
R2 QC min	0	[mL]
R2 QC max	25	[mL]
R2 EQP index	1	
Result 3 (R3) name	B	
R3 hide	Yes	
R3 min	0	[mL]
R3 max	25	[mL]
R3 QC min	0	[mL]
R3 QC max	25	[mL]
R3 EQP index	2	
Result 4 (R4) name	FOS	
R4 hide	No	
R4 min	0	[mg/L CH ₃ COOH]
R4 max	82000	[mg/L CH ₃ COOH]
R4 QC min	0	[mg/L CH ₃ COOH]
R4 QC max	82000	[mg/L CH ₃ COOH]
R4 equation	500*((R3*4*1.66)-0.15)	
Result 5 (R5) name	FOS/TAC	
R5 hide	No	
R5 min	0	
R5 max	10	
R5 QC min	0	
R5 QC max	10	
R5 equation	(500*((R3*4*1.66)-0.15))/R1	

4.2. Recommendation for modification of settings

Mainly for analysis time reduction, some parameters can be adjusted. It has to be noticed that the impact can be a loss of precision on the results.

A pH measurement can be added before the titration.

In order to follow the ISO 10523:2008 standard set the **Active** fields of **Sample homogenization** and **pHi** sections to **Yes**. Or, if your SOP requires stirring during pH measurement, activate only the **pHi** section and set a stirring speed, for example 25%.

5. Procedure

5.1. Electrode / Titrant calibration

If the electrode and/or titrant calibration is required, see section **9 Appendix: Electrode and titrant calibrations**.

5.2. Sample analysis

Put 5 mL (weighed as 5 g) of roughly filtered substrate into a 150 mL PP beaker, dilute with 50 mL of deionized water and add a magnetic stir bar. Place the beaker onto the titrator and launch the FOS/TAC value application on the main menu. If it is enabled, an initial pH measurement is performed and then the titration starts. At the end of the analysis, rinse the probe and the addition tip.

6. Results

6.1. Displayed Results

At the end of the titration the following results are available:

1. pHi: initial pH measured before titration if enabled
2. TAC in mg/L as CaCO₃
3. FOS in mg/L as CH₃COOH
4. FOS/TAC value without unit

6.2. Results calculation

TAC calculation:
$$TAC = \frac{A \times C_{tit} \times 50045}{V_{smp}}$$

FOS calculation:
$$FOS = ((B \times 4 \times 1.66) - 0.15) \times 500$$

Where:

A = Volume of titrant at pH 5.0 (mL)

C_{tit} = Concentration of titrant (eq/L)

V_{smp} = Volume of sample (5 mL fixed by the FOS formula, for the Nordmann method)

B = Volume of titrant by difference at pH 4.4 (mL) = volume of titrant at pH 5.0 – volume of titrant at pH 4.4

7. Examples of FOS/TAC determination

The results described below are indicative and obtained for a given sample in optimized conditions respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

7.1. FOS/TAC determination of water treatment plant sample

Results for 10 determinations of a water treatment plant sample with default settings.

Sample: 5 mL of substrate + deionized water

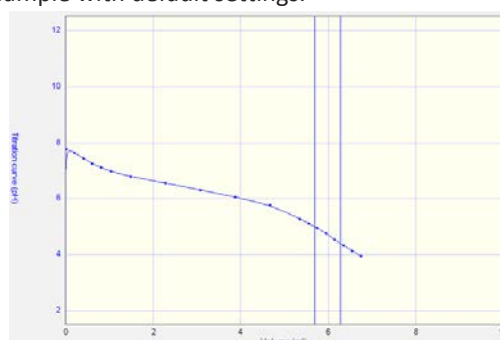
Temperature of analysis: Room temperature

Mean value of FOS/TAC: 0.320

Standard deviation: 0.008

Relative standard deviation: 2.65%

Curve pH versus volume of titrant:



8. Bibliography

- McGhee T. J., 1968, *A Method For Approximation of the Volatile Acid Concentrations in Anaerobic Digesters, Water and Sewage Works, April 1968, Vol. 115, pp. 162-166.*
- Voß E., Weichgrebe D., Rosenwinkel, K. H., 2009, *FOS/TAC-Deduction, Methods, Application and Significance, Internationale Wissenschaftskonferenz „Biogas Science 2009 – science meets practice“, LfL-Bayern, 2-4. 12.09, Erding.*

9. Appendix: Electrode and titrant calibrations

To increase accuracy of the FOS/TAC determination, it is recommended to perform an electrode calibration every week. For the titrant, it is recommended to calibrate it after a bottle change or after a long storage time.

9.1. Electrode calibration

9.1.1. Electrode and buffers

Electrode: Combined pH electrode with temperature sensor, Intellical PHC805.

pH standards: Color-coded pH 4.01, pH 7.00 and pH 10.01 are set by default. It is possible to change them according to your SOP (refer to the full user manual for more details).

9.1.2. Electrode calibration settings

By default the electrode calibration is done with the parameters described below:

Name	Default parameter	Unit
Application		
Application name	FOS-TAC value	
Electrode		
Recommended	PHC805	
Calibration frequency	7	[Day]
Stability criterion	0.050	[pH/min]
Max. stability time	300	[s]
Stirring speed	25	[%]
Stirring duration	15	[s]
Calibration mode	Auto	
Buffer set	Color-coded 4.01, 7.00 and 10.01	

Note: The parameters are defined to calibrate the electrode following the ISO 10523:2008 standard which recommends stirring the buffer before the measurement, and to stop stirring during measurement. If your SOP requires stirring during the measurement, set the **Stirring duration** to 0 s.

The calibration mode is set as **Auto** by default, but two other options are also available: **Fixed** and **Manual**. Refer to the full user manual for more details.

9.1.3. Electrode calibration procedure

It is recommended to calibrate the electrode at a temperature close to the sample temperature.

Pour a sufficient amount of buffer into a beaker so that the electrode dips into the solution. Add a magnetic bar and launch the calibration sequence. Rinse the electrode between each buffer. The electrode can be calibrated with up to five different buffers.

9.1.4. Calibration results

At the end of the series of buffers, the following results are displayed:

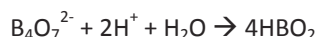
- Slope in mV/pH
- Slope in % compared with theoretical slope (-59.16 mV/pH)
- Offset in mV

The acceptance limits for the slope are 97-102% and between - 30 and + 30 mV for the offset.

9.2. Titrant calibration

9.2.1. Principle

The strong acid used as titrant has to be calibrated with Borax which reacts with H⁺ ions according to:



9.2.2. Electrode and reagents

Electrode: Combined pH electrode with temperature sensor, IntelliCAL PHC805
Titrant: Sulfuric acid, H₂SO₄ 0.1 eq/L solution in deionized water
Standard: Borax powder (M = 381.37 g/mol)
Deionized water

9.2.3. Settings

The following parameters have been set to use about 5 mL of titrant for the calibration.

Name	Default parameter	Unit
Application		
Application name	FOS-TAC value	
Advisable syringe	10 mL	
Electrode		
Recommended	PHC805	
H₂SO₄ 0.1 N method: Calibration		
Active	Yes	
Calibration frequency	0	[Day]
Stirring speed	25	[%]
Predose volume	2	[mL]
Delay	5	[s]
Max. vol. stop point	8	[mL]
Ordinate stop point	2.0	[pH]
Stop on last EQP	Yes	
IP1 min. ordinate	4.5	[pH]
IP1 max. ordinate	6.5	[pH]
Min. titrant conc.	0.9000	[eq/L]
Max. titrant conc.	0.1100	[eq/L]
Standard name	Borax	
Standard amount	95	[mg]
Min. amount	75	[mg]
Max. amount	115	[mg]
Concentration	99.5	[%]
Molar weight	381.372	[g/mol]

9.2.4. Procedure

Accurately weigh approximately 95 mg of Borax in a beaker and add a sufficient amount of deionized water to cover the electrode and the delivery tip with solution. Put in a magnetic stir bar, place the beaker on the titrator and dip the electrode and delivery tip into the solution. Launch the titrant calibration sequence.

9.2.5. Result

The result is expressed as eq/L concentration of the titrant and based on the following formula:

$$C_{\text{H}_2\text{SO}_4} = \frac{m_{\text{borax}} \times C_{\text{borax}}}{M_{\text{borax}} \times V_{\text{H}_2\text{SO}_4} \times 50}$$

Where:

$C_{\text{H}_2\text{SO}_4}$: Titrant concentration in eq/L

m_{borax} : Mass of Borax in mg

C_{borax} : Concentration of Borax in % (purity of borax powder)

M_{borax} : Molar weight of Borax = 381.37 g/mol

$V_{\text{H}_2\text{SO}_4}$: Volume of H_2SO_4 at the equivalence point in mL

The calibration result can be accepted if five determinations give a result with a relative standard deviation of less than 0.5%.

9.2.6. Example of titrant calibration

Results for 10 titrant calibrations using the default parameters:

The results described below are indicative and obtained for a given titrant in optimized conditions respecting good laboratory practices. These indicative values are sample-dependent, electrode-dependent and operating cell-dependent.

Standard: 95 mg of 99.5% Borax powder dissolved in 100 mL of deionized water

Temperature of analysis: Room temperature

Concentration of titrant: 0.0997 eq/L

SD: 0.0001 eq/L

RSD: 0.09 %

Titration curve:

