Determination of FOS TAC value in Biogas plants
Use

The determination of the volatile organic acids (FOS) and total inorganic carbon (TAC) or buffer monitor the fermentation process in biogas reactors.

Determination of FOS/TAC value is performed as an endpoint titration to two pH endpoint using sulphuric acid. The FOS, TAC and the ratio of FOS/TAC are automatically calculated and displayed.

The FOS TAC method is stored as default method inside the TitroLine® 6000/7000/7750 titrators

Appliances

Titrator: TL 6000_M2/50 consists of

- Basic device
- Magnetic stirrer TM 235
- 50 mL exchange unit WA 50, with brown glass bottle for titrant complete
- pH combination electrode A 7780 DIN ID

Electrodes

- see above
- Calibration: DIN buffer pH= 4.00 and pH= 7.00
Reagents

- Titrant: H2SO4 0.05 mol/L
- Titer: Possible with TRIS (Tris (hydroxymethyl)-aminomethan)

Description

Calibration

The pH combination electrode is calibrated in technical buffer pH=4.00 and pH= 7.00 or in DIN buffer pH= 4.01 and pH= 6.87.

Example of the calibration documentation:

<table>
<thead>
<tr>
<th>Buffers used</th>
<th>Measured values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH buffer 1: TEC_4.000</td>
<td>pH buffer 1: TEC_4.000 165.6 mV / 23.4 °C</td>
</tr>
<tr>
<td>pH buffer 2: TEC_7.000</td>
<td>pH buffer 2: TEC_7.000 -11.2 mV / 23.0 °C</td>
</tr>
</tbody>
</table>

Calibration data

- Slope: 99.4 % / -58.8 mV/pH
- Zero point: pH 6.81 / -11.2 mV
- Temperature: 23.4 °C (a)
- Date and time: 07.03.13 / 15:04

Determination of the exact concentration of the standard solution (option)

The exact concentration of the H2SO4 0.05 mol/L titrant can be determined using a titrimetric standard Tris (hydroxymethyl)-aminomethan. TRIS is dried in a desiccator before the titer determination overnight at room temperature.

The standard method for HCl/H2SO4 titrant (*titer HCl) is stored as a default method inside the TitroLine® 6000/7000/7750 titrators. With EDIT/F3 - Default method you can load this method. It is only necessary to change the name of the method and the factor F2 in the calculation formula:

Factor 2 (F2): 1000.0000
Factor 1 (F1): 1.0000

The factor 1 (F1) should be changed to 2.
In a 100 or 150 ml, 0.2 to 0.3g TRIS are weighed accurately and dissolved in 60/80 mL of dist. water with stirring. It is titrated with H2SO4 0.05 mol/L.
Documentation example for standard titration of H₂SO₄/HCl with TRIS

**Titration Data**

<table>
<thead>
<tr>
<th>Sample ID:</th>
<th>TRIS</th>
<th>Weight:</th>
<th>0.1038 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start pH:</td>
<td>pH 9.590</td>
<td>End pH:</td>
<td>pH 3.864</td>
</tr>
<tr>
<td>Start temperature:</td>
<td>25.0 °C (m)</td>
<td>End temperature:</td>
<td>25.0 °C (m)</td>
</tr>
<tr>
<td>Zero point:</td>
<td>pH 6.83 / -10.0 mV</td>
<td>Slope:</td>
<td>100.5 % / -59.5 mV/pH</td>
</tr>
<tr>
<td>EQ:</td>
<td>8.560 ml / pH 4.849</td>
<td>Titre:</td>
<td>0.1001 mol/l</td>
</tr>
</tbody>
</table>

**Calculation Formula**

\[
\text{Titre: } \frac{(W^2 + F2)}{(E1-B) + M^2 + F1} \rightarrow M103
\]

<table>
<thead>
<tr>
<th>Weight (W):</th>
<th>man</th>
<th>Factor 2 (F2):</th>
<th>1000.0000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank value (B):</td>
<td>0.0000 ml</td>
<td>Factor 1 (F1):</td>
<td>1.0000</td>
</tr>
<tr>
<td>Statistics:</td>
<td>Off</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Method for standard titration of H2SO4/HCl with TRIS

**Method data overall view**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method name</td>
<td>Titre HCl</td>
</tr>
<tr>
<td>Method type</td>
<td>Automatic titration</td>
</tr>
<tr>
<td>Measured value</td>
<td>pH</td>
</tr>
<tr>
<td>Titration mode</td>
<td>Dynamic</td>
</tr>
<tr>
<td>Dynamic</td>
<td>Steep</td>
</tr>
<tr>
<td>Measuring speed / drift</td>
<td>Normal</td>
</tr>
<tr>
<td>minimum holding time</td>
<td>02 s</td>
</tr>
<tr>
<td>maximum holding time</td>
<td>15 s</td>
</tr>
<tr>
<td>Measuring time</td>
<td>02 s</td>
</tr>
<tr>
<td>Drift</td>
<td>20 mV/min</td>
</tr>
<tr>
<td>Initial waiting time</td>
<td>0 s</td>
</tr>
<tr>
<td>Titration direction</td>
<td>Decrease</td>
</tr>
<tr>
<td>Pretitrination</td>
<td>Off</td>
</tr>
<tr>
<td>End value</td>
<td>2.500 pH</td>
</tr>
<tr>
<td>EQ</td>
<td>On (1)</td>
</tr>
<tr>
<td>Slope value</td>
<td>Steep</td>
</tr>
<tr>
<td>Value</td>
<td>700</td>
</tr>
</tbody>
</table>

**Dosing parameter**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosing speed</td>
<td>100 %</td>
</tr>
<tr>
<td>Maximum dosing volume</td>
<td>50.00 ml</td>
</tr>
<tr>
<td>Filling speed</td>
<td>30 s</td>
</tr>
</tbody>
</table>

**Unit values**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit size</td>
<td>20ml</td>
</tr>
<tr>
<td>Unit ID</td>
<td>100390005</td>
</tr>
<tr>
<td>Reagent</td>
<td>HCl 0.1 mol/L</td>
</tr>
<tr>
<td>Batch ID</td>
<td>no Charge</td>
</tr>
<tr>
<td>Concentration [mol/L]</td>
<td>0.10070</td>
</tr>
<tr>
<td>Determined at</td>
<td>12/05/11 19:18:45</td>
</tr>
<tr>
<td>Expire date</td>
<td>08/18/12</td>
</tr>
<tr>
<td>Opened/compounded</td>
<td>09/10/11</td>
</tr>
<tr>
<td>Test according ISO 8855</td>
<td>05/10/11</td>
</tr>
<tr>
<td>Last modification</td>
<td>09/13/12 14:35:18</td>
</tr>
</tbody>
</table>

**Device information**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device</td>
<td>Titroline 7000</td>
</tr>
<tr>
<td>Serial number</td>
<td>00012</td>
</tr>
<tr>
<td>Software version</td>
<td>1230</td>
</tr>
</tbody>
</table>

*date: 28.2.2012*
Titration of the sample

The sample is either centrifuged 20 min or filtrated before use. It is also important that a larger amount of the sample is homogenized before filtration/centrifugation. The sample should be treated always in the same manner.

20 ml of the filtrated sample (or less) are pipetted in a beaker and diluted with water that the pH electrode and titration tip can immerse correctly.

Select the FOS TAC method and start the titration.

**Result example:**
Method data

Method name: FOS TAC
End date: 08.01.13
Titr. duration: 7 m 9 s
End time: 17:39:42

Titr. data

Start pH: pH 7.148
Start temperature: 25.0 °C (m)
Zero point: pH 6.88 / -6.7 mV
EP1: 17.950 ml / pH 5.000
EP2: 20.788 ml / pH 4.400

Pattern: 20.00000 ml
End pH: pH 4.390
End temperature: 25.0 °C (m)
Slope: 97.5 % / -57.7 mV/pH
TAC: 4487.50
FOS: 2280.54
FOS/TAC: 0.51

Calculation formula

TAC: $\frac{(F1/V)\cdot EP1\cdot F2}{F3\cdot F4}$
FOS: $\frac{(F1/V)\cdot (EP2\cdot EP1)\cdot F3\cdot F4\cdot F5}{F6\cdot F7}$
FOS/TAC: $\frac{(F6\cdot F7)}{(F8\cdot F9)}$
Factor 1 (F1): 20.00000
Factor 2 (F2): 250.0000
Factor 4 (F4): 0.1500
Factor 5 (F5): 500.0000
Factor 6 (F6): 2280.54 (FOS)
Factor 8 (F8): 4487.50 (TAC)
Pattern (V): 20.0000 ml (f)
Factor 3 (F3): 1.6000
Factor 7 (F7): 1.0000
Factor 9 (F9): 1.0000
Statistics: Off
The method is available as default method in the TL 6000/7000/TL 7750 titrator and ready to use.

**Method data overall view**

- **Method name**: FOS TAC
- **Method type**: Automatic titration
- **Measured value**: pH
- **Titration mode**: End pt.
- **Linear steps**: 0.050 ml
- **Created at**: 01/08/13 17:30:29
- **Last modification**: 01/08/13 17:32:28
- **Damping settings**: None
- **Documentation**: GLP

**Measuring speed / drift**: Normal
- **minimum holding time**: 02 s
- **maximum holding time**: 15 s
- **Measuring time**: 02 s
- **Drift**: 20 mV/min

**Initial waiting time**: 0 s
- **Titration direction**: Decrease
- **Preparation**: Off

**Endpoint 1**: pH 5.000
- **delta endpoint 1**: pH 0.400
  - **Endpoint delay 1**: 5 s

**Endpoint 2**: pH 4.400
- **delta endpoint 2**: pH 0.400
  - **Endpoint delay 2**: 5 s

**Dosing parameter**
- **Dosing speed**: 40 %
- **Maximum dosing volume**: 50.00 ml
- **Filling speed**: 30 s

**Unit values**
- **Unit size**: 20 ml
- **Unit ID**: 10039005
- **Reagent**: HCl 0.1 mol/L
- **Batch ID**: no Charge
- **Concentration [mol/l]**: 1.66666
- **Determined at**: 01/07/13 21:41:57
- **Expire date**: 09/18/12
- **Openness/compounded**: 09/10/11
- **Test according ISO 8655**: 05/10/11
- **Last modification**: 01/07/13 13:42:17
If you have any questions on the application, you can feel free to contact us.

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