Determination of organic in biogas reactors

Figure 1: Biogas plant in Adensen near Hildesheim, Germany (Photograph: Lorey)

Acetic acid (CH_3COOH)) is a suitable substrate for nearly all types of bacteria and is therefore commonly used during aerobic or anaerobic wastewater treatment in sewage treatment plants. Other examples worth mentioning are processes during biological phosphorus elimination or denitrification. Acetic acid is also the preferred substrate during methane production in biogas reactors.

Biogas reactors are presently mushrooming in rural areas (Figure 1). In Germany the political course chosen in the revised Renewable Energy Act (Erneuerbare Energien Gesetz, EEG) has prompted many farmers to become energy suppliers. Corn silage, rye silage (whole plant) or other energy crops can be used as raw materials for the production of methane gas under anaerobic bacterial digestion conditions. Also, many new bioreactor plants have been designed and put into operation for the utilisation of waste residues. The resulting methane can be converted into electricity. For combined heat and power generation in particular, this promises high-energy efficiency and, thanks to various grants and subsidies, high capital gains.

Organic acids crucial for methane production

Unfortunately, methane production does not always proceed as easily as expected. For many reasons, methane production can be slowed down. In this case, acidified bacteria are producing short-chain organic acids at a much faster rate than methane-producing bacteria can break them down. This causes accumulation of different organic acids of which higher concentrations of propionic acid (C_2H_5COOH) in particular slow down the biogas production process due to its toxic effect on methane-producing bacteria.

Determination of organic acids is therefore of growing interest. Analysis of steam volatile acids according to DIN 38414-S19, which is based on phosphoric acid distillation with water vapour and subsequent titration with sodium hydroxide solution, is not very effective as this method does not distinguish between the 'good' acetic acid and the 'bad' propionic acid. Furthermore, the use of the cuvette test, based on the formation of complex-forming fatty acid esters and subsequent photometric determination, is not of much help.

GC for liquid samples

Chromatographic analysis offers an excellent and straightforward option requiring no time-consuming sample preparation for differential analysis of steam volatile organic aids.

Materials present in biogas reactors can generate large amounts of dry residue, which may require a multistage sample preparation procedure including centrifugation. Under normal conditions, sample preparation only requires

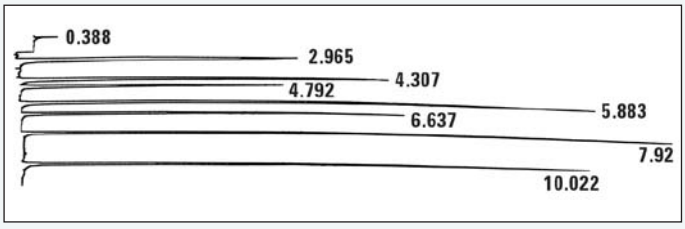
acids in wastewater and

GC for liquid samples

filtration using a standard one-way syringe fitted with a 0.45 µm nylon filter holder. A volume of 0.7 mL of a highly diluted pH 1.5 phosphoric acid solution is added to GC vials (1.5 mL, screw cap N8 with conical bore and red-white PTFE-silicone seals).
An equal amount of the filtrate (0.7 mL) is subsequently pipetted into the GC vials. The GC vials must be promptly closed (red PTFE side towards the liquid) in order to prevent the meanwhile non-dissociated acids from escaping via the gas-phase. The sealed and cooled samples and standards can be stored for up to one week, provided that the seals remain unbroken.

For the standard solution, seven acids are weighed out:
- Acetic acid
- Propionic acid
- Isobutyric acid
- Butyric acid
- Isovalerianic acid
- n-Valerianic acid
- Caproic acid.

Concentrations between 100 and 800 mg/L are recommended. As acetic acid, propionic acid and butyric acid are usually present in higher concentrations, these should be used in slightly higher concentrations in the standard. Separation is carried out on an FFAP column using helium as carrier gas. The Permabond FFAP-DF capillary column, (25 m x 0.32 mm, Macherey-Nagel) and the Zebron ZB-FFAP capillary column (30 m x 0.32 mm, 0.25 µm df, Phenomenex) were tested successfully so far. The split ratio was 1:100. The temperature programme is started at 84 °C and held for 3 minutes, then increased by 6 °C/min up to 120 °C, which is held for approximately 3 minutes. Depending on the liner and split ratio used, sample volumes up to 3 µL are injected. A sample chromatogram (Figure 2) resulting from separation on a Shimadzu GC-9A with FID, after automatic injection via an AOC-17 autosampler equipped with the AOC-1400 sample cooling rack, was generated using the Shimadzu CR3A integrator. The GC system and the integrator are meanwhile 20 years old but still offer reliable operation.



CHROMATOGRAM 1

PKNU	TIME	AREA	IDNO	CONC.	NAME
1	2.965	4750	1		Acetic
2	4.307	4358	2		Propionic
3	4.792	2551	3		Isobutyric
4	5.833	5036	4		Butyric
5	6.637	2825	5		Isovalerianic
6	7.920	4575	6		n-Valerianic
7	10.022	4176	7		Caproic

Figure 2: Calibration chromatogram with standard solution

Trouble-free method

The method is trouble-free and applicable for municipal sewage, most industrial wastewaters as well as discharges and sludges in anaerobic plants. Regular comparison with the results according to DIN 38414-S19, after stoichiometric conversion of the gas chromatographically determined sum in acetic acid equivalents, resulted in very good agreement with the results, even for concentrations up to 10,000 mg/L. Problems can arise at high concentrations (≥ 2000 mg/L) of D- or L-lactic acid in the substrate, which can occur for instance in dairy farm or slaughter house wastewater. Such disturbances can be recognised from the reproducibly strong baseline drift or an unusually strong peak tailing. When in doubt, a control experiment can be carried out using the cuvette test and/or titrimetric analysis according to DIN 38414-S19 as described above. The lactic acid content is relatively simple to determine enzymatically, but cannot be detected via gas chromatographic analysis.

The propionic acid content should be tested regularly in biogas reactors. Propionic acid can lead to reactor operation problems already at concentrations < 500 mg/L. Using the method described above, problem-free acquisition of the spectrum of steam volatile organic acids is possible in less than 15 minutes.

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