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# Online measurement of fatty acids in biogas plants with Near Infrared Reflexion Spectroscopy (NIRS)

A promising possibility for monitoring the biological process in biogas fermenters is offered by applying measurement systems based on the principles of Near Infrared Reflection Spectroscopy (NIRS). Still missing in this respect is a comprehensive calibration of substrate-specific contents within the fermenter and achieving this is the aim of the project described. Volatile fatty acids were introduced into two laboratory-scale biogas fermenters. Their increase in the substrate was measured spectrally and via gas chromatography. The spectra data collection time was increased to simulate a higher sample volume in front of the sensor and thus improve the calibration model. With a lower number of outliers the robustness of the model increased permitting more precise estimation of unknown samples.

**Keywords**

NIRS, biogas, volatile fatty acids, multivariate data analysis, support vector regression

**Abstract**

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So that biogas plants work as efficiently as possible they are often equipped with security systems e.g. leakage monitoring, condensate separator, low pressure control, and much more. This is because a stable biological process is indispensable wherein the four process steps of biogas production run parallel to one another without any obstruction. This allows methane production potential to be exploited in the most efficient way. However, the possibilities for continuous monitoring of these biological processes within the fermenter have, up until now, been limited in comparison to the systems mentioned above. In this respect the fundamental question is: How to recognise whether the process in the fermenter is hardly working or running optimally? In most cases one determines this by taking a sample of the substrate from the fermenter and determining volatile fatty acid content and buffering capacity (FOS/TAC) through wet-chemical testing in laboratory. However, the situation may have long changed once again before results arrive, and problems in the process may have brought methane production in the fermenter to a halt.

A promising possibility for real time monitoring of the biological process online is offered by application of a measurement system based on the principles of Near Infrared Reflection Spectroscopy (NIRS). Online monitoring in biogas plants using NIRS has been already described many times [1; 2; 3].

The biological research platform (Ministry for Rural Areas, Food and Consumer Protection) was established within the framework of the Baden-Württemberg Future Offensive IV programme. Within the cluster „Unterer Lindenhof“ a regulating and control system for online monitoring of renewable raw products biogas plants was conceived in cooperation with the Hohenheim University State Institute of Agricultural Engineering and Bioenergy with the University of Stuttgart (ISWA, Institute for Sanitary Engineering, Water Quality Management and Waste Management). The aim of the total project is the application of NIRS in the monitoring and management of process stability within the fermenter, and for regulation in the case of process fluctuations.

## The principle of Near Infrared Reflection Spectroscopy (NIRS)

NIRS is a rapid and non-destructive method of determining substrate-specific characteristics from samples using the physical-optical characteristics of the substrate. Light waves are directed onto chemical compounds within the fermentation substrate. The measured absorption, calculated from light wave reflection, enables indirect conclusions on fatty acid concentration and composition. In the same way silage components and their dry matter content can be determined via NIRS. Light from a lamp is radiated onto the sample through a small sapphire window. The light reflected from the substrate is relayed to the NIR detector via sensor and fibre optics (**figure 1**). In the detector the intensity of the reflected light in the near infrared wavelength range (760–1700 nm) is measured in a diode-array spectrometer and given as a spectrum. The resultant spectra are then stored in a databank.

The NIRS measurement and evaluation principle is presented in **figure 2**. For the NIRS calibration are required the sensor-detected spectra and the analyses of the samples taken at the same time. These samples are analysed in the laboratory to determine the parameters to be calibrated for (all volatile fatty acids – acetic, propionic, valeric, butyric and caproic as well as FOS/TAC results and content of dry matter and organic dry matter). Only the combination of the reference data and the associated spectra gives, over a statistical evaluation (multivariate data analysis), the NIRS estimation model, e.g. with „support vector regression" (SVR). A calibration must continually be expanded and improved with new data to ensure the provision of reliable estimations of unknown samples. The more parameters that are to be estimated, the greater the required amount of data.

## Material and methods

To determine the condition of substrate in biogas plants online NIRS measurement was first of all carried out with two horizontal semi-continuously powered 400-litre experimental biogas fermenters in the laboratory. Both fermenters are equipped with a NIR spectrometer from the company TENIRS in Kiel. With each fermenter a sensor is screwed into the front via a 2-inch sleeve so that there is direct sensor contact with the substrate within the fermenter. Directly adjacent to the sensor is a ball valve to allow withdrawal of samples. The technical/biological parameters of the experimental biogas fermenters are given in the following text. For comparison purposes one of the fermenters was operated in the thermophilic temperature range at 52 °C and the second in the mesophilic temperature range at 41 °C. Both fermenters were fed once daily with the same amount of substrate comprising maize silage, manure and water. The hydraulic retention time represented 35 days in each case with a volumetric loading of 3 kg organic dry matter/($m^3$ • day).

Fig. 1


*TENIRS sensor, ready for mounting in a measuring pipe*

## Experimental process

For calibration of the NIRS measurement system based on acids in the fermenter substrate, several experiments were conducted with acetic acid and then propionic acid fed into the fermenters, as well as both in combination and with acetate. The aim was to achieve starting values at different concentration levels from 1 to 10 g/kg acid. The reduction of the acids was documented over several days through sampling from every hour to every three hours with simultaneous recording of the spectra. The samples taken were analysed in the laboratory to determine their content of volatile fatty acids as well as respective FOS/TAC values. Data evaluation took place with „support vector regression" (SVR) with radial kernel function [4].

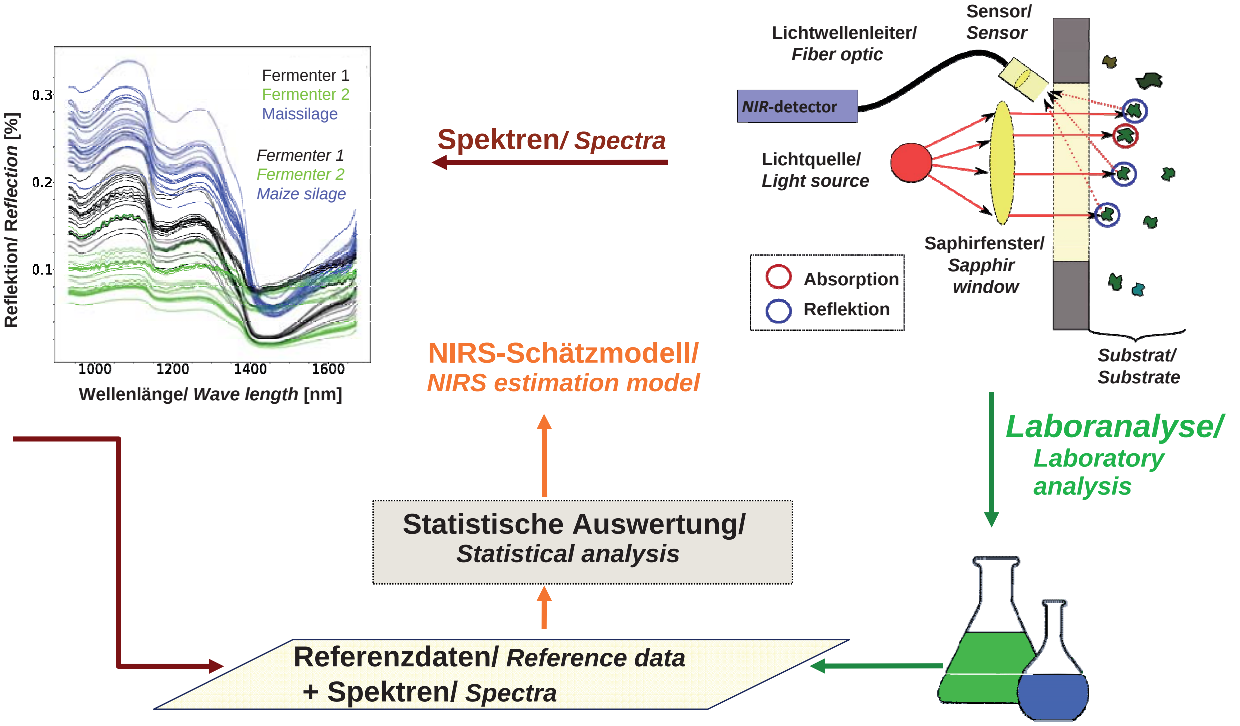
## Results and discussion

For clarity purposes only the results from the thermophilic fermenter are presented here. Referenced laboratory zero values were wrongly assessed by the NIRS measurement system, possibly because of the overlapping substrate effect. For this reason most samples identified in the laboratory as having an acetic acid concentration of under 0.5 g/kg were already defined in the calibration model as outliers (samples to the left of the green line in **figure 3**). Too many of the non-usable samples ended-up as outliers thus preventing the achievement of a good model (marked red in **figure 3**). Outliers can be due to the most different causes: mistakes in taking samples and in their further processing, malfunctions in spectra analysis. However, the number of outliers in a calibration model should be as low as possible. The high number of outliers in the here presented calibration could be because the volume of samples flowing by the front of the sapphire window of the sensor during measurement was too low. In order to investigate this, a further calibration model was developed from the same experiment using the available data whereby the spectral data record of every single sample was increased from 2 min. (recording of 600 spectra) up to 12 min. (recording of 3600 spectra). This allowed the simulation of larger sample volumes in front of the sensor. The calibration was thereby visibly improved in that with less outliers a more suitable model could be created (**figure 4**). While the imprecision remained within the 0–0.5 g/kg range, the model robustness was increased through the elimination of the marked outliers.

## Conclusions

Near Infrared Reflection Spectroscopy appears well suited for prediction of volatile fatty acid content between 0.5 and 8 g/kg in biogas fermenters. However, it is absolutely necessary that calibration models be improved and further developed. The calibrations presented here show clearly that the robustness of the models could be increased through the number of spectra used per measurement point. This indicates that during a mea-

Fig. 2




*NIRS calibration: development of a NIRS estimation model with statistical analysis with reference data and corresponding spectra; TENIRS, 2009 [5], modified by A. Stockl*

surement the substrate volume flowing past the sensor has a decisive influence on the precision of the calibration. Possibly the positioning of the sensor can also have an effect in this respect. For this reason further experiments are planned to determine the best sensor positioning and to vary the flow speed of the substrate in order to achieve the best possible calibration results. Only with a robust calibration can samples with unknown concentrations of volatile fatty acids be precisely determined over a wide concentration spectrum.

## Literature

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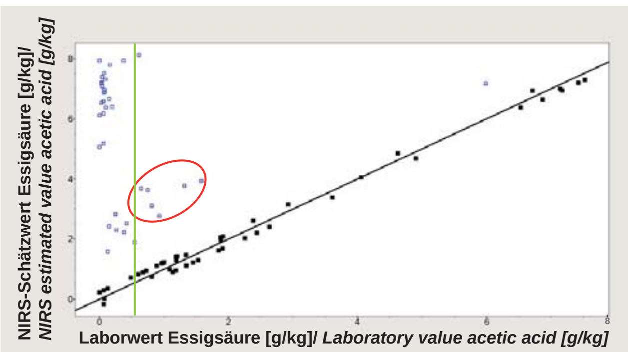
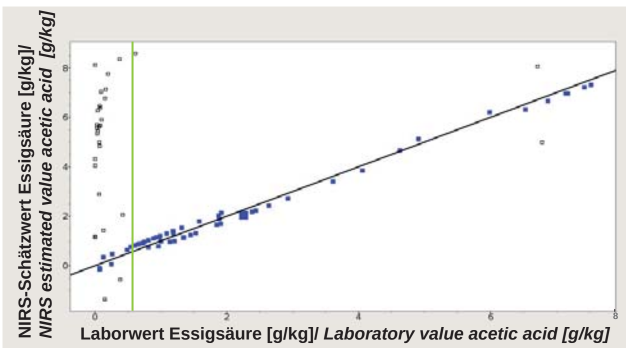
Fig. 3




84 samples; ▫ 36 outlier; RMSEP 0,48; RMSEC 0,21; Range/ SEP 15,77

*NIRS calibration model for acetic acid in the thermophilic digester (analysis of 600 spectra for one measuring point each over a period of two minutes)*

Fig. 4




84 samples; ▫ 30 outlier; RMSEP 0,56; RMSEC 0,20; Range/ SEP 13,18

*Improved NIRS calibration model for acetic acid in the thermophilic digester (analysis of 3600 spectra for one measuring point each over a period of twelve minutes)*

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