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Transfer of a near infrared spectroscopy laboratory application to an online process analyser for in situ monitoring of anaerobic digestion

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HIGHLIGHTS

- We confirm the potential for robust in situ monitoring of anaerobic digestion.
- Total volatile fatty acid concentration can be visualised by near infrared spectroscopy.
- Validation of the models was performed on an independent spectra time series.
- Piecewise direct standardisation allows pooling of spectra from different instruments.

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ABSTRACT

A near infrared (NIR) spectroscopy online process analyser was used for in situ monitoring of anaerobic digestion of energy crops and livestock residues. Spectra were measured on a lab instrument and subjected to piecewise direct standardisation for a spectra transfer. The transfer was used in conjunction with samples for which data was recorded online for the partial least squares regression of volatile solids, ammonium, total inorganic carbon, and volatile fatty acids parameters in the fresh matter of a digester slurry. Validation was performed on independent time series spectra. The results confirmed that the procedure is robust in terms of NIR monitoring of these parameters in order to support the high potential for cross-linking different spectrometers, which may help in making this technology practical.

1. Introduction

Organic matter selectively absorbs near infrared (NIR) radiation, and this can yield information about its molecular bonds, the foremost of which are the CH, OH, and NH bonds (Siesler, 2008). A common assumption regarding spectroscopic measurements in the NIR region is that the amount of light that is absorbed by the sample at different wavelengths is proportional to the concentration of its chemical functional groups (Griffiths and Dahm, 2008). The concentrations of the functional groups are in turn related to the concentrations of the different physicochemical parameters which allows for their quantitative determination. The use of NIR technology to quantitatively measure parameters that are usually obtained from wet chemistry analyses requires a model for extracting this information from spectroscopic signals, such as multivariate calibration (Feudale et al., 2002). After the models have been independently (externally) validated, they can be used for analysing unknown samples (Bouveresse and Campbell, 2008). However, several situations can arise in which an NIR model can be invalid. One scenario involves the occurrence of changes in the physical or chemical constitution of the sample that has to be analysed. In the case of anaerobic digestion (AD) monitoring, variations in pH, temperature, and analyte concentration of a slurry can change the hydrogen bonding within the sample, which in turn complicates the interpretation of overlapping NIR spectral bands (Shenk et al., 2008; Workman and Burns, 2008). Furthermore, the main challenge of a feedstock-robust calibration is the complex nature of the NIR spectra, which are characterised by inter-constituent interactions and the strong influence of a sample's scattering properties on its spectral signature (Osborne and Fearn, 1986). One strategy that can be used to avoid erroneous estimations is

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to incorporate these expected variations into the calibration (Swierenga et al., 2000). Therefore, fewer sources of variation need to be controlled in the future applications of the model. In a study by Krapf et al. (2011), the potential for developing feedstock-robust calibrations was tested for the following parameters using partial least squares (PLS) regression: volatile solids (VS), ammonium (NH_4–N), total inorganic carbon (TIC), and volatile fatty acids (VFA). External validation of these lab models showed that an increase in the calibration robustness did not result in a relevant loss of its accuracy in making estimations (Krapf et al., 2012).

Another scenario refers to the practical limitation of using an NIR model when the samples to be estimated are measured on an instrument other that the one for which the calibration was developed (Feudale et al., 2002). One example is the situation where the calibration is performed on a lab instrument. If future samples are to be measured with an online process analyser (Heise and Winzen, 2002; Næs et al., 2002), the calibration that was carried out on the lab instrument is not applicable for estimating samples recorded under these new conditions because strongly biased estimations can occur (Despagne et al., 2000; Feudale et al., 2002). This happens because the interactions between light and the sample are generally different in different optical spectrometer systems, thereby causing variations in the band shapes and intensities of the spectra (Shenk, 2004). To avoid having to carry out a full recalibration of the model under these new conditions, standardised methods can be applied to modify the response function of one instrument (or application) such that it is similar to that of the other instrument. Different strategies can be used for this purpose: the regression coefficients of the prediction model can be standardised, or the values or the spectral responses can be predicted by mathematical manipulation (Feudale et al., 2002). The latter strategy is the one most commonly used (Næs et al., 2002), and of the different methods that are available for this strategy, piecewise direct standardisation (PDS) is probably the most used (Feudale et al., 2002). The goal of PDS is to generate a transfer function that is developed from samples that have been measured in parallel on different instruments. When deriving the transformation matrix, each data point on the one instrument is reconstructed from data that is located within a small window on the other instrument (Heise and Winzen, 2002). This is accomplished by developing a local multivariate transfer model between the spectral windows of the host and the central point in each corresponding spectral window on the master (Despagne et al., 2000). The requirements for such standard samples have been extensively discussed, as well as the methods for their selection from a larger set of samples (see references in Bouveresse and Campbell, 2008). In principal, the samples that are used for building the transfer function should optimally represent the spectral variability in the sample set that is to be transferred (Forina et al., 2007). Furthermore, standard samples should be similar when they are measured on different instruments in that they should be physically and chemically stable (Bouveresse and Campbell, 2008). These requirements can be limited by practical considerations and the success of PDS depends on the extent to which the standard samples meet these criteria. In the present study, the transfer and subsequent independent validation of an earlier reported lab application to an online process analyser for monitoring in situ AD parameters of agricultural biogas plants is described.

2. Methods

2.1. Use of samples that were obtained from the lab instrument

The experiments of the lab application included samples that had been collected from 38 large-scale biogas plants and 14 lab digesters that contained a feedstock composition of energy crops and livestock waste as described in more detail in Krapf et al. (2012). The samples ($N = 431$) were scanned offline with a Fourier Transform (FT)-NIR spectrometer (Vector 22/N, Bruker Optics, Ettlingen, Germany) using diffuse reflection ($\log(1/R)$) in the 12,000–3700 cm^{-1} region. The temperatures of the samples were randomly changed from 35 to 40 °C during the recordings. Not all the samples were used in the present study, so that spectral redundancies in the PLS model could be avoided (Kessler, 2007). Therefore, a cluster analysis (Næs et al., 2002; 30 clusters, 20 iterations, Kendall's Tau) was performed with the lab samples in the 9000–4100 cm^{-1} region of the first derivation spectra (Unscrambler 9.8, Camo, Oslo, Norway). From each cluster, seven samples were selected to evenly span the total VFA range within one cluster. If the number of samples in one cluster was <7, the missing samples were taken from adjacent clusters. This resulted in the selection of 210 samples that were used for further data analysis.

2.2. Online spectral recordings

Digester A had a working volume of 2500 L and was operated for 90 days at 35–42 °C by using maize silage as a feedstock. Organic loading rates (OLR) that were measured as VS of up to 9 kg m^{-3} - d^{-1} were maintained for 10 consecutive days, which caused the total concentration of VFA to increase to 20 g kg^{-1} fresh matter (FM) indicating overloading. To speed up digester recovery, on day 68, 500 L of the digester content was substituted with material from a biogas plant that was fed with silage from maize and a grass-legumes mixture, and 300 L was exchanged with cattle manure. This treatment resulted in subsequent recovery of the AD process and the experiment was stopped after stable AD conditions were re-established (total VFA <1 g kg^{-1} FM). To be able to make spectral recordings, the digester was equipped with an external-loop system (Högemann GmbH, Garrel, Germany) and the slurry was pumped through a metal pipe (50 mm in diameter) to provide continuous loop circulation. A sapphire window (40 mm in diameter) was fitted to an upstream section of the pipe on which a measuring head (Q-412A, Bruker Optics) was mounted at a distance of 10 cm (measuring spot, 10 mm). The measuring head was connected to an FT-NIR spectrometer (Matrix-F, Bruker Optics) via fibre optics for online recording of the log(1/R) spectra by an InGaAs detector (12,400–4000 cm^{-1}). The spectra were averaged for 45-s intervals (144 scans, 16 cm^{-1} resolution) using Opus 6.5 software (Bruker Optics). For sampling ($N = 48$), the slurry was removed via a ball valve that was closely situated behind the measuring head during these 45-s intervals. The volume of the primary sample was 40 L, from which a 5-L sub-sample was taken before a 0.5-L sample was bottled for wet chemistry analyses.

Digester B had a liquid volume of 250 L and was operated for 26 days at 32–48 °C. The inoculum was composed of maize silage, grass and cattle manure. During the experiment, feeding up to an OLR of 10 kg m^{-3} d^{-1} was carried out to generate a strong variation in the AD process, using silage from maize, a grass–clover mixture, and wheat straw. The digester content was partly replaced by material from four plants, which were fed with maize silage, as well as grass, green rye, and manure from cattle and poultry in different proportions. The spectrometer was the same as that for digester A and the sapphire window on which the measuring head was mounted was directly integrated into the digester wall. During sampling ($N = 49$), the primary samples were collected via a ball valve that was located close to the window. The volume that was removed during 45 s of sampling was 10 L, from which a 0.5-L reference sample was directly taken.

Digester C was used for external validation and had an effective capacity of 150 L. It was stirred by a paddle agitator (140 min^{-1}) during the 26 days of fermentation. An inoculum of a biogas plant