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Research Paper

Effects of measurement technique and sample preparation on NIR spectroscopy analysis of livestock slurry and digestates

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Near infrared spectroscopy (NIRS) was used to analyse livestock slurries and digestates. The purpose was to evaluate the influence of sample preparation, reading set-up and sample temperature during NIR scanning on digestates and livestock slurry samples. To obtain accurate and reproducible values of total solids (TS), total kjeldahl nitrogen (TKN), total ammoniacal nitrogen (TAN) and volatile fatty acids (VFA) contained in dairy and pig slurry and digestate, a total of 36 samples were analysed from different farms in Lombardy, Italy. Three sample preparations (filtration, homogenisation and a raw control), two reading set-ups (petri dish and optical fibre) and three sample temperatures (10, 25 and 35 °C) were tested during NIR scanning. Results showed that analysis of livestock slurries and digestates by NIR spectrophotometry is influenced by sample preparation. Both filtered and homogenised samples generally showed higher correlations (r^2) and ratio of standard error of performance to standard deviation (RPD) ($0.79 < r^2 > 0.98$ and $2.26 < RPD > 6.99$ for filtered samples; $0.30 < r^2 > 0.97$ and $1.24 < RPD > 6.31$ for homogenised samples) than raw samples ($0.03 < r^2 > 0.95$ and $1.05 < RPD > 4.73$), but the better sample preparation was filtration. Spectral acquisition through petri dishes was slightly more accurate than through optical fibre. No observable effects on spectral analysis were caused by altering temperature in the range of 10–35 °C.

1. Introduction

The advantages of using near infrared spectroscopy (NIRS) for compositional analysis are numerous, prompting its widespread usage. NIRS generates no wastes and can provide concentration estimates for multiple components quickly once calibrations have been developed for the components of interest (Reeves & Van Kessel, 2000).

This technique has been used to determine the chemical composition of livestock manure. Most of such applications

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Nomenclature

ALK	alkalinity
EC	electrical conductivity
NIRS	Near Infrared Spectroscopy
PCA	principal component analysis
PLS	partial least squares regression
r2	coefficient of determination
RMSECV	root mean square error in cross validation
RMSEP	root mean square error in prediction
RPD	ratio of performance to deviation
SD	standard deviation
TAN	total ammoniacal nitrogen
TK	total potassium
TKN	total kjeldahl nitrogen
TP	total phosphorus
TS	total solids
VFA	volatile fatty acids
VS	volatile solids

have evaluated the total solid (TS), total kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) in manure to produce the immediate results required for more adequate and environmentally friendly agronomic management of the product.

Some authors used raw samples of dairy or swine slurry, poured into a polyethylene bag and scanned in reflectance at a controlled temperature (Table 1). Although temperatures were controlled, a range of temperatures have been used; Millmier et al. (2000) scanned samples within the range of 23–27 °C, Ye, Lorimor, Hughburgh, Zhang, and Hattey (2005) at used room temperature, and Reeves and Van Kessel (2000) at 4 °C.

Raw samples of swine slurry have been analysed also in reflectance by inserting an optical fibre into the sample (Saeys, Mouazen, & Ramon, 2005), as well as in transflectance using a sample cell at 4 °C (Malley, Yesmin, & Eilers, 2002). The results for TS and TKN were similar, while those for TAN were poorly correlated (Saeys et al. 2005) or contradictory (Malley et al. 2002) (Table 1).

Instead of using raw (unprocessed) samples, Sorensen, Sorensen, and Birkmose (2007) applied NIRS on homogenised samples of dairy and swine slurries for the determination of TS, TKN and TAN. The samples were poured into a polyethylene bag and measured in reflectance (Table 1).

The models for using NIRS data to estimate other nutrients such as phosphorus (P) and potassium (K) have disagreed. Some studies reported that it was not possible to predict P content in manure samples (Malley et al. 2002; Ye et al. 2005), but Xing, Chen, and Han (2008) and Saeys et al. (2005) reported that total P could be approximately determined by NIRS, while Millmier et al. (2000), Reeves and Van Kessel (2000) and Reeves (2001) reported that NIRS did not perform well in predicting either P or K. These contrasting results could be explained by the fact that NIRS may provide indirect or surrogate predictions for P (Chen, Xing, & Han, 2009) and K (Reeves, 2001) based on the inter-correlation among organic components.

Another application of NIRS in manure management is for estimating the content of the main volatile fatty acids (VFAs) formed during anaerobic digestion of slurry, such as acetic, butyric and propionic acid.

Monitoring changes in VFAs can give valuable information about the status of the anaerobic process and thus assist in managing a digester by, for example, optimizing the feeding (Finzi, Oberti, Riva, & Provolo, 2014).

The measurement of VFAs was proposed originally for digestates, but it could also be an interesting indicator of the odour potential and biological stability of dairy and pig slurry (Hansen, Kai, & Møller, 2006; McCrory and Hobbs, 2001; McGinn, Janzen, & Coates, 2003). Several studies showed a satisfactory application of NIRS to predict VFAs content in digestates under different experimental settings with mean squared errors in prediction of the order of 0.5–2 g l^{-1} (Table 2) (Hansson, Nordberg, & Mathisen, 2003; Holm-Nielsen, Andree, Lindorfer, & Esbensen, 2007; Holm-Nielsen & Esbensen, 2011; Krapf, Gronauer, Schmidhalter, & Heuwinkel, 2011; Lomborg, Holm-Nielsen, Oleskowicz-Popiel, & Esbensen, 2009; Nordberg et al. 2000). Jacobi, Moschner, and Hartung (2009), Lomborg et al. (2009) and Holm-Nielsen et al. (2007, 2011) reported significant partial least squares prediction (PLS) models for total VFA, acetic and propionic acid using a tool for at-line and on-line measurements of the complex composition of bio-slurries during biological conversion processes, using transflexive embedded NIR sensor (TENIRS) system. This system analysed homogenised samples scanned in transflectance.

Nordberg et al. (2000) and Hansson et al. (2003) used an optical fibre and NIRS to predict both acetic and propionic acid concentration in organic substrates during anaerobic digestion at 37 °C, while Hansson et al. (2003) predicted only propionic acid concentration. However, Krapf et al. (2011) used raw samples poured into a cuvette and scanned in reflection at 35–40 °C, and reported that NIR could predict the content of total VFA (r^2 0.92–0.94) in digester sludge, but could not produce accurate models for acetic and propionic acid.

The research cited above focused primarily on the estimative capacity of NIRS without appropriate comparison of the possible effects that the procedural steps of the measurement technique may have on results. For example, there is evidence that the temperature at which samples are scanned might affect the spectral shape, shifting the peaks (Kemeny, 2007). As no "standard procedure" yet exists, variations can occur in sample preparation, the method used for optical readings, and the temperature at which samples are analysed.

Knowledge of the influence of procedural steps on NIRS predictions is relevant both to comparing the results of different studies and to defining the design characteristics of simplified NIRS devices for making field measurements. In fact, up to now, almost all the applications of NIRS on manures and digestates have used standard laboratory equipment that is unsuitable for direct applications on farms or for in-situ monitoring of digesters.

Furthermore, the different approaches used to make NIR measurements discourage identification of the most reliable and suitable technique for transfer to field use because no comparative studies, based on an appropriate experimental design, have been conducted.

The aim of this study was to fill this gap by evaluating the effect of different measuring techniques on NIRS estimation