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Technical aspects concerning the detection of animal waste nutrient content via its electrical characteristics

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HIGHLIGHTS

- ▶ Manure electrical conductivity sensors can have problems of duration and reliability.
- ▶ We study the corrosion resistance of 3 metals and a prototypal probe through Response Surface Modelling.
- ▶ The most suitable materials are: stainless steel (mass −1.8%, 15-mm dist.), brass (mass −13.0% max at 35 mm).
- ▶ The regression laws of the probe reach $R^2 \geqslant 0.74$ considering: voltage drop, dry matter, temperature.
- ▶ Not considering the dry matter the estimates are still reliable ($R^2 \geqslant 0.66$) for $T \geqslant 20$ °C.

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ABSTRACT

The variables influencing corrosion of three metals (galvanised steel, stainless steel, brass) usable for a manure nutrient probe were examined, identifying the best material for field applications. The nutrients in 18 liquid manures were then estimated through the voltage drop between the terminals of a prototype probe.

Response Surface Modelling gave the regression functions relating each investigated response only to the statistically-significant factors.

After 168 h in the manure, it was determined that: stainless steel was the most suitable material for very close electrodes (mass: −1.8% at 15 mm), brass can be used with any inter-electrode distance (mass: −13.0% maximum at 35 mm).

The prototype probe gave reliable estimates ($R^2 \geqslant 0.744$) of N_{tot}, N_{amm}, P_{tot}, K_{tot} when dry matter and temperature were also accounted for in the regression analysis. Not considering dry matter but just electronically-detectable quantities (temperature, voltage drop), the estimates were only reliable ($R^2 \geqslant 0.656$) above 20 °C.

1. Introduction

The surface and underground water pollution that occur as a result of nutrient leakage from manure fertilisers (Vidal et al., 2000), together with the requirement in the related European norms, evidence the need for determining the exact nutrient content of manure (Provolo et al., 2009).

The analytical methods used for this determination, although very accurate, require time to perform and, more importantly, must be conducted by qualified personnel in equipped laboratories. These limitations do not meet the requirements for agronomic interventions, i.e., rapid analysis and ease of data acquisition. A possible solution to these difficulties would therefore be the development of rapid and simplified analytical methods (Van Kessel and Reeves, 2000).

Many studies have examined the use of Near Infrared Spectroscopy (NIRS), obtaining significant results, developing highly accurate calibration procedures and defining the possible limits of the applicability of this technique (Reevesi and Van Kessel, 2000; Saeys et al., 2005; Huang et al., 2008; Changwen et al., 2010). However, these systems are very delicate and prohibitively expensive. Recent research has therefore focused on alternative, less expensive systems.

In particular, many studies have been published in the last 30 years that examined the correlation of numerous chemical characteristics of manure (properties that can generally only be determined using laboratory analyses) with other physical properties

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Nomenclature

Symbol	Definition, units
Δm^+	Absolute mass loss of the positive electrode of a cell (g)
Δm^-	Absolute mass loss of the negative electrode of a cell (g)
Δm_{tot}	Absolute mass loss of both electrodes of a cell (g)
$\%\Delta m^+$	Percentage mass loss of the positive electrode of a cell (%)
$\%\Delta m^-$	Percentage mass loss of the negative electrode of a cell (%)
$\%\Delta m_{tot}$	Percentage mass loss of both electrodes of a cell (%)
ΔE_i	Energy that is supplied by a battery in a generic time interval Δt_i (J)
Δt_i	Generic time interval (s)
a_0	Interception coefficient in a third-degree full-cubic regression model
AC	Alternating current
a_i	Coefficient of the linear terms in a third-degree full-cubic regression model ($1 \leqslant i \leqslant k$, $k \geqslant 2$)
a_{ii}	Coefficient of the quadratic terms in a third-degree full-cubic regression model ($1 \leqslant i \leqslant k$, $k \geqslant 2$)
a_{iii}	Coefficient of the cubic terms in a third-degree full-cubic regression model ($1 \leqslant i \leqslant k$, $k \geqslant 2$)
a_{ij}	Coefficient of the 2nd order interaction terms in a third-degree full-cubic regression model ($1 \leqslant i \leqslant j \leqslant k$, $k \geqslant 2$)
a_{ijh}	Coefficient of the 3rd order interaction terms in a third-degree full-cubic regression model ($1 \leqslant i \leqslant j \leqslant h \leqslant k$, $k \geqslant 2$)
D	Nominal electrode diameter (resistance test) (m)
DC	Direct current
DM	Dry matter (%)
e	Specific energy supplied by the battery during an experiment (Wh g^{-1})
EC	Manure electrical conductivity (S m^{-1})
E_{tot}	Total energy supplied by the battery during an experiment
I	Electric current (A)
J	Current density (A m^{-2})
K_{tot}	Manure total potassium (TK) (mg $kg_{DM}{}^{-1}$)
ℓ	Distance between the electrodes (m)
MDL	Method detection limit
MN	Province of Mantova (Italy)
N_{amm}	Manure ammoniacal nitrogen (AN) (mg kg^{-1})
N_{tot}	Manure total Kjeldahl nitrogen (TK) (mg kg^{-1})
PD	Province of Padova (Italy)
ρ	p-value (-)
P_i	Power supplied by the power supply in a generic time instant t_i (W)
P_{tot}	Manure total phosphorus (TP) referred to DM ($\%_{DM}$)
R^*	Internal circuits equivalent resistance (Ω)
R_m	Manure equivalent resistance (Ω)
S	Area of the electrode surface in contact with the manure (m^2)
T	Manure temperature (°C)
t_i	Generic time instant (s)
V	Voltage drop indicated by the system (nutrient content estimation test) (V)
V^*	Measured voltage drop (nutrient content estimation test) (V)
V_{ps}	Power supply voltage (V)
VR	Province of Verona (Italy)
x_i	Generic independent variable in a third-degree full-cubic regression model ($1 \leqslant i \leqslant k$, $k \geqslant 2$)
y	Generic predicted response in a third-degree full-cubic regression model

(i.e., density, dry matter-DM, electrical conductivity-EC) which can be easily determined (Tunney, 1979; Overcash et al., 1983; Scotford et al., 1998b; Martínez-Suller et al., 2008). These correlations are applicable not only to bovine (Chen et al., 2009a) and swine manure (Chen et al., 2009b) but also to chicken dung (Huang et al., 2011).

Among the examined parameters, EC is the best-suited for obtaining indirect estimates of the ammoniacal and total nitrogen content (Moral et al., 2005; Suresh et al., 2009). The determination coefficients obtained in the cited studies are very high, although rather variable, depending on the type of livestock stalling, geographical area and animal species (Parera i Pous et al., 2009, 2010b). These coefficients are therefore useful for determining the nutrient content (Reijs et al., 2003) and for calculating the volumes of manure that should be distributed to obtain the desired nutrient dose (Parera i Pous et al., 2010a). The proposed correlation laws are linear in the majority of studies, but other reported relationships are polynomial and multi-parametric (Parera i Pous et al., 2010b; Suresh and Choi, 2011; Yagüe et al., 2012). One publication proposes the use of artificial neural network models to determine the nutrient content of dairy cattle manure (Chen et al., 2008).

While many authors believe that these methods can be used to rapidly analyse nutrient contents at a fixed farm installation (Scotford et al., 1998a; Suresh and Choi, 2011), efforts have recently been made to implement these systems directly in slurry tankers (Scotford et al., 1999). This research has been conducted with the aim of raising the automation level of the control systems on such vehicles. In this way, with data on the nutrients in the manure load, the operator would only be required to input the maximum dose of nitrogen to be distributed on the field (e.g., based on Directive 91/676/EEC).

Problems, primarily related to the lifespan of the instrument, may arise during the transition of a technology from the laboratory to the industrial field. Although such issues are common, they are not often discussed. The electrified metal components constituting the sensitive portion of the probe can be damaged by both the manure, which is chemically very corrosive, and by electrochemical phenomena. The circuit formed by the manure and an electrified probe is similar to an electrolytic cell in which the liquid manure is the electrolyte and the electrode that is connected to the positive pole of the battery corrodes.

Given the encouraging results obtained with the first prototypes of these electrical probes (Provolo and Martínez-Suller, 2007), our aim was to develop a new probe that is (i) smaller (and, therefore, easily installed on new and existing slurry tankers), (ii) capable of also measuring the nutrient content of digestates and, most important, (iii) capable of achieving the same level of sensitivity and reliability (in terms of durability) as previous electrodes.

Because calibration curves must be plotted for each new probe geometry, taking into account both the distance between the electrodes and the extension of the electrode surface that is in contact with the manure, the design of a new probe involves two main tasks:

- investigation of the optimal metal, taking into account its contact with the manure and its active electrification;
- calibration of the new probe with respect to nutrient content measurements.

For the present analysis, the probe was developed in collaboration with ARVAtec s.r.l (Rescaldina – Milano, Italy).

The aims of this study are: (i) to identify the optimal metal to be used for the construction of a probe that can quantify nutrient