

Friedrich Weißbach, Elmenhorst, and Cornelia Strubelt, Parchim

Correcting the Dry Matter Content of Grass Silages as a Substrate for Biogas Production

During the process of determining DM content in silages, volatile compounds (fermentation acids and alcohols) are lost. Therefore, the DM content measured in the conventional way has to be corrected afterwards. If uncorrected or incompletely corrected, calculations on nutrient contents, as well as specific biogas yields will give false results, causing experimental data to be misleading [2, 3]. A sufficiently exact calculation of the volatile compounds is only possible with a full chemical analysis of all the fermentation acids and alcohols contained in the silages. After an equation for corrected DM values for maize silages is proposed [6], an improved and substrate specific equation for DM correction for grass silage is recommended here.

Knowledge on the degree of volatility of all the individual fermentation products during drying under defined drying (volatilization coefficients) is required in order to enable the correction of DM content of silages. Data on volatilization coefficients have already been published earlier [1, 4]. It was shown in these studies that the volatilization coefficient of an individual compound can normally be determined by measuring and comparing the contents in the fresh silage sample and in the respective drying residue. The only exception is lactic acid. Due to a specific chemical reaction of lactic acid (formation of lactide) which is facilitated through dehydration by heat treatment and affected by various drying conditions, the decrease of lactic acid content during drying can be higher than its transfer into gas phase.

In those experiments, volatilization of certain alcohols remained unclear as these compounds could not be separated out by chromatography at that time [5]. This applies especially to alcohols with more than one hydroxyl-group. As a consequence of the use of special silage additives, enhanced formation of 1,2-propanediol is caused in silages. A volatilization coefficient of 77 % for 1,2-propanediol which frequently occurs in

maize silage has recently been determined [6], whereas data are still lacking for 2,3-butanediol which can be found at a high incidence in grass silages.

The aim of the study was to determine the range of concentration of volatile fermentation products in grass silages as well as their volatilization coefficients in order to propose an improved equation for the correction of DM content of grass silages with special regard to mentioned two alcohols.

Material and Methods

A set of 182 grass silage samples from commercial farms was used, representing a wide range of DM level and substantial differences in fermentation quality. Information on use of silage additives and storage length upon sampling were not available. All silages were analysed for potentially volatile fermentation products in fresh and dried samples.

DM content was determined by preliminary drying at moderate temperature and subsequent final drying of the milled sample at 105 °C for 3 hours. In previous investigations [1, 4, 6], drying residues were analysed after final drying at 105 °C for 3 hours. In the experiments described here, however, the

Table 1: Frequency of occurrence, concentration and volatilization percentage of fermentation products from grass silages (n = 182)

	Incidence %*	Concentration in silage g kg ⁻¹ FM			Volatilization coefficient %	
		Mean	Range	Standard deviation	Mean	Standard deviation
Acids:						
Acetic acid	100	8.27	2.53 ... 20.67	3.38	78	7
Propionic acid	100	0.45	0.05 ... 6.89	0.68	78	15
Iso-butyric acid	63	0.19	0 ... 1.41	0.27	84	9
Butyric acid	91	2.06	0 ... 17.02	3.20	88	13
Iso-valeric acid	98	0.36	0 ... 3.31	0.39	71	13
Valeric acid	55	0.10	0 ... 1.48	0.21	93	11
Caproic acid	68	0.19	0 ... 3.03	0.44	92	12
Lactic acid	100	14.63	1.06 ... 34.10	7.50	10	6
Alcohols:						
Ethanol	100	2.50	0.16 ... 23.59	3.04	99	2
Propanol	49	0.20	0 ... 4.70	0.57	100	0
Butanol	14	0.01	0 ... 0.20	0.03	100	0
1,2-Propanediol	70	0.60	0 ... 8.12	1.15	77	17
2,3-Butanediol	80	0.26	0 ... 2.62	0.39	87	14

* Proportion of samples with a content of the individual compound of > 0.05 g kg⁻¹ FM

Prof. Dr. agr. habil. Friedrich Weißbach was head of the Institute of Grassland and Forage Research in the former Federal Research Centre of Agriculture (FAL) in Brunswick, Germany, until 1999 and works now as senior consultant;

e-mail: prof.f.weissbach@web.de

Cornelia Strubelt is a university qualified chemist and head of the Analytical Laboratory for Agriculture and Environment, Bgg Deutschland GmbH, in Parchim, Germany.

Keywords

Biogas, grass silage, dry matter, correction for volatile compounds

Literature

References can be called up under LT 08421 per Internet www.landtechnik-net.de/literatur.htm.

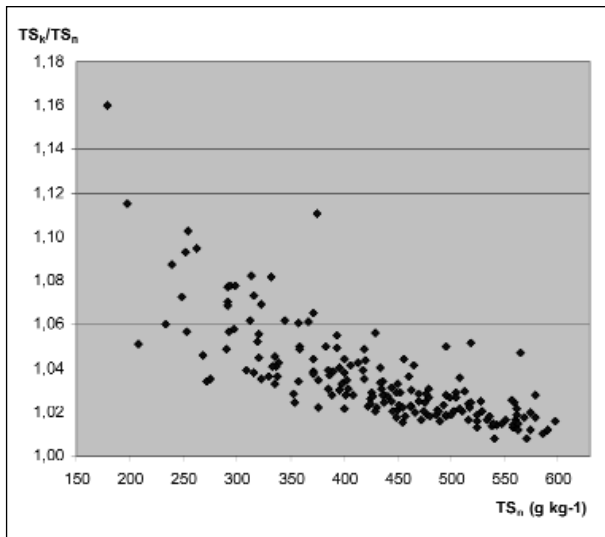


Fig. 1: Relationship between measured DM content (DM_n) and volatilization losses during sample drying from grass silages indicated by the quotient DM_c/DM_n

air-dry milled samples were used for analysis of fermentation products after had been submitted to an additional drying process at 70 °C over night (approximately 16 hours).

Results and discussion

DM content of the analysed silages ranged between 179 and 597 g kg⁻¹ (mean: 428 g kg⁻¹), and pH varied between 3.8 and 6.1 (mean: 4.8). Results of the analyses for volatile fermentation products are summarized in Table I.

As in maize also in grass silages, acetic acid was found to represent the vast proportion of short chain fatty acids, which are known to be highly volatile. But in addition to acetic and propionic acid, butyric acid and their higher homologues (valeric and caproic acid) were determined here at substantial frequency and sometimes in substantial concentrations as well. It has been known that volatility of all these acids during drying depends on pH. The lower pH of the silage, the higher is the volatility [1, 5]. The high variability of pH explains the high standard deviation of the volatilization coefficients for these acids in grass silages. The variability of the volatilization coefficient was at least markedly higher than recently reported for maize silages [6]. The error of the use of a generalized mean volatilization coefficient can be avoided, if the silage pH is taken into account. Volatilization coefficient (VC) for the total of low fatty acids in grass silages can be estimated by using the following substrate-specific regression:

$VC [\%] = 105 - 0.059 \text{ pH}$ ($S_R = 5.7$)
Volatility of lactic acid does not depend on pH and is generally low. The average volatilization coefficient for lactic acid in this study was 10 % which agrees reasonably well with previous investigations from which a mean value of 8 % was generalised [1].

Grass silages on average contain smaller amounts of alcohols than maize silages. But ethanol was shown to be the major alcohol also in grass silages, and its concentration can reach substantial levels. Propanol and in particular butanol occur at markedly lower frequency. All these alcohols with one hydroxyl-group evaporate completely during drying. Regarding 1,2-propanediol, which was found to occur in grass silages in similar concentrations like in maize silages, an average volatility of 77 % could be confirmed. As expected, incidence of 2,3-Butandiol was higher in grass silages than previously found in maize silages. This study enables for the first time to determine the volatilization coefficient of this compound. On average, 87 % of the 2,3-butandiol initial present in silage are lost during drying.

In summary, contents of potentially volatile fermentation products in grass silages are extremely variable, whereas the variation of volatilization percentage of the individual compounds under defined drying conditions is relatively small.

Conclusions and recommendations

Grass silages may, as reported for maize silages, contain substantial concentrations of volatile organic compounds, which possess biogas forming potential and therefore must not be neglected in measuring the specific gas yield potential. Therefore, a complete chemical analysis of grass silages is absolutely necessary, if the specific gas yield is determined by fermentation tests. The use of simplified methods for DM correction without determination of individual fermentation products, e.g. methods based on the relationship between DM content and losses of volatiles during drying of silage samples can result in big errors.

Figure 1 illustrates the calculated losses of volatiles in the 182 grass silage samples used in this study which were derived from the direct comparison of the content of fermentation products in fresh silage and its respective dried sample. Losses averaged about 4 %, but were found to be as high as 16 %. On account of differing fermentation intensity in silos which results in variation in the content of fermentation products and is affected by DM content of the ensiled grass, a clear tendency could be observed towards higher losses at lower DM levels. In individual cases, however, losses in silages of the same DM concentration can differ by up to 10% as consequence of different fermentation pattern.

Based on the complete analysis of fermentation products, the following equation for calculating the corrected DM content (DM_c) of grass silages from the non-corrected DM content (DM_n) measured by oven drying is recommended:

$$DM_c = DM_n + (1.05 - 0.059 \text{ pH}) \text{ FA} + 0.08 \text{ LA} + 0.77 \text{ PD} + 0.87 \text{ BD} + 1.00 \text{ OA} [\text{g kg}^{-1} \text{ FM}]$$

where is:

FA = total of low fatty acids ($C_2 \dots C_6$)

LA = lactic acid

PD = 1,2-propanediol

BD = 2,3-butanediol

OA = total of other alcohols ($C_2 \dots C_4$)

Concentrations for all individual compounds have to be fitted in the equation in the dimension g per kg fresh matter (FM).

The equation is valid for defined drying conditions (preliminary drying at 60 - 65 °C until constant weight and subsequent final drying at 105 °C for 3 hours).

As a consequence of DM correction, all other DM-based concentrations, e.g. nutrient contents, have to be corrected as well. All parameters which are typically subjected to direct analysis in the dried sample and usually expressed as percent of DM_n (e.g. crude ash), must be corrected by multiplication of the value with the quotient of DM_n/DM_c . All fractions which are obtained by difference calculation, such as organic DM (oDM), must be calculated once more using the values expressed as percent of DM_c .

Acknowledgments

The authors wish to express their gratitude to the NAWARO® BioEnergie AG for funding this project and the results presented here.

Literature

- [1] *Berg, K., und F. Weißbach*: Untersuchungen zur vollständigen Erfassung des Trockensubstanzgehaltes von Silagen. 1. Mitt.: Ermittlung der Stoffverluste bei der Trocknung von Silageproben. Arch. Tierernährung 26 (1976), S. 661-672
- [2] *Mukengele, M., und H. Oechsner*: Einfluss der Silierung auf den spezifischen Methanertrag bei Mais. Landtechnik 62 (2007), H. 1, S. 20-21
- [3] VDI-Richtlinie 4630 „Vergärung organischer Stoffe“. VDI-Gesellschaft Energietechnik, Düsseldorf, 2006, ICS 13.030.30; 27.190, S. 59
- [4] *Weißbach, F., und K. Berg*: Untersuchungen zur vollständigen Erfassung des Trockensubstanzgehaltes von Silagen. 2. Mitt.: Methoden zur Bestimmung und zur Korrektur des Trockensubstanzgehaltes. Arch. Tierernährung 27 (1977), S. 69-84
- [5] *Weißbach, F., und S. Kuhla*: Stoffverluste bei der Bestimmung des Trockenmassegehaltes von Silagen und Grünfütter: Entstehende Fehler und Möglichkeiten der Korrektur. Übers. Tierernährung 23 (1995), S. 189-214
- [6] *Weißbach, F., und C. Strubelt*: Die Korrektur des Trockensubstanzgehaltes von Maissilagen als Substrat für Biogasanlagen. Landtechnik 63 (2008), H. 2, S. 82-83