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(Metod för korrigering av VFA-förlust vid bestämning av torrhalt i biomassa)

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*"Catalyzing energygas development
for sustainable solutions"*

SGC Svenskt Gastekniskt CenterAB

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Malmö 2013

Martin Ragnar
Verkställande direktör

Swedish Gas Technology Centre, SGC

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Malmö, Sweden 2013

Martin Ragnar
Chief Executive Officer

Foreword

This project, "*Method for correction of VFA loss in determination of dry-matter",*
was initiated by the department of FoU Biogas at Tekniska verken i Linköping AB.
The project group consisted of Cecilia Vahlberg, Erik Nordell, Lina Wiberg
(Tekniska verken in Linköping AB) and Anna Schnürer (Swedish University of
Agricultural Sciences, SLU). The project started in May 2012 and was completed
in February 2013 when this report was published.

The project had a reference group consisting of the following representatives:

Tobias Persson   SGC (program director)
Irene Bohn   NSR AB
Catarina Jonasson   EON Gas Sverige AB

Summary

There is an increasing demand for bio-methane, as a renewable energy source. To accomplish a stable, efficient and optimal biogas production, it is important to monitor the digestion process. Imbalance in the digester may be caused by e.g. insufficient process-follow up and poor characterization and control of the substrates properties. Parameters often used to evaluate the stability and the efficiency of the biogas production process are the hydraulic retention time (HRT), organic loading rate (OLR), the specific gas production and the degree of degradation. These parameters (except for the HRT) are all calculated based on the volatile solids (VS) content, which is the organic part of the dry-matter (DM) content.

A common technique to determine the DM content is by oven-drying. This is a very simple and robust method where water is evaporated and the dry matter of the sample remains. However, a disadvantage of the method is that volatile molecules (in addition to water) are lost during the drying. Volatile substances include among others, volatile fatty acids (VFAs) and alcohols. This may result in an underestimation of the DM content, and subsequently also an underestimation of the VS content. Consequently, this will result in errors in all the parameters that are calculated based on DM and VS.

In this project, the focus was to understand the evaporation of VFAs from different substrates used for biogas production and digestates (biofertilizer) during the DM-analysis, by oven-drying at 105°C for 20 hours.

First, a method for analyzing the concentration of VFAs in oven-dried materials by first dissolving the dried material in MilliQ water was confirmed. This method was used throughout the project.

Moreover, the majority of the dissolved total organic carbon that was lost during the DM-analysis was confirmed to be VFAs ($\approx$75%). Consequently, determination quantification of the evaporation of VFA from substrates and digestates during DM-analysis are therefore of greatest importance.

In this study four different biogas substrates and three digestates were included in the laboratory research. Results showed that the majority of the VFAs in all four substrates (with low pH) were lost during the DM-analysis using the oven-drying method ($\geq$95%). Moreover, the evaporation was not depending on the initial VFA concentration. In the four substrates, the VFA evaporation will result in significant errors in both the DM and VS analysis of 3-30 %. Errors in parameters calculated based on the observed results varied in size correspondingly to DM and VS. The error increases with increasing ratio between VFA/DM; meaning that the high VFA concentration in relation to the DM content increased the error. It was also shown that the degree of degradation could both be under-estimated and overestimated.

The conclusion of the study was that there are of greatest importance compensate for the VFA evaporation which occurs during the DM-analysis. This assumes that the VFA content of the substrate should be measured for more correct results of DM and VS. Two methods are suggested to compensate for the VFA evaporation during the DM-analysis. The methods can easily be applied if the DM, VS and VFA content of the substrates or digestates are analyzed.

Sammanfattning på svenska

Intresset för biogas som en förnybar energikälla har under de senaste åren ökat i Sverige. För att kunna upprätthålla en stabil och optimal rötningsprocess är det av väsentlig betydelse att drift- och processdata följs upp och övervakas på ett tillfredställande sätt. Dessvärre suboptimeras ibland biogasproduktionen på grund av bristande processövervakning. Driftstörningar kan leda till processinstabilitet med minskad biogasproduktion som följd. En förutsättning för en bra processuppföljning är att kontinuerligt kontrollera och karaktärisera substratet. De vanligaste parametrarna för substratanalys är torrsubstansen (TS, även kallat DM) och glödförlusten (VS, även kallad GF). Ofta analyseras även koncentrationen av VFA och ammoniumkväve, alkalinitet och pH i rötkammaren, men inte alltid kontinuerligt i substraten. Den organiska fraktionen av ett material (VS) mäts ofta som en andel av torrsubstanshalten; VS används för att oberoende av vatteninnehållet i ett prov, kunna uppskatta den organiska belastningen eller gasproduktionen från ett visst substrat.

Det finns en rad olika processparameterar som används för att övervaka och utvärdera stabiliteten i biogasprocessen. De vanligaste processparametrarna som övervakas är; uppehållstid (HRT), organisk belastning (OLR), specifik gasproduktion och utrötningsgrad. Dessa parametrar (HRT undantaget) baseras på substratets organiska innehåll, dvs. VS och därmed indirekt TS-halten. TS och VS-halten kan bestämmas med flera olika typer av analysmetoder. Inom VA- och biogasbranschen är det vanligast att TS-halten bestäms genom ugnstorkning vid kontrollerade förhållande, med avseende på tid och temperatur. Enligt den svenska standarden SS 02 81 13 (SIS, 1981) kan TS-mätning ugn appliceras på t.ex. avloppsvatten, slam och sedimentprover. Vid bestämning av TS-halt i ett slam rekommenderas en torktid på 20 timmar vid 105°C. Det finns dock en rad alternativa metoder till ugnstorkning som inte är vanliga vid mätning av slam men desto vanligare inom andra industrier så som livsmedelsindustrin och skogsindustrin t.ex. Karl-Fisher titrering, infraröd spektrometri och mikrovågs-torkning. Vid flertalet biogasanläggningar används även en snabbmetod för TS-mätning som baseras på torkning av materialet med infraröd strålning (värme).

TS-mätning med hjälp av ugnstorkning används frekvent då den är mycket enkel, billig och kräver inte heller någon avancerad utrustning. Vidare är det enkelt att analysera VS i direkt anslutning till analys av TS i ugn genom att glödga TS-provet vid 550°C i 2 timmar (SIS, 1981). Bestämning av TS-halt genom ugnstorkning är dock förknippat med vissa antaganden; dels att endast vatten avgår vid upphettningen av materialet, dels att avgången av vatten är den samma i alla typer av material och dels att vi inte får några reaktioner i materialet under upphettningen som påverkar resultatet. Eftersom biogassubstrat innehåller flertalet flyktiga föreningar som t.ex. alkoholer och flyktiga fettsyror finns det därför en ökad risk för avgång av dessa eller liknande föreningar då TS-halten bestäms vid ugnstorkning. Detta kan således leda till att felaktigt värde på TS-halten och därmed även ett felaktigt VS-värde erhålls och processparametrar som beräknas baserat på dessa blir missvisande.

Det huvudsakliga syftet med projektet var att utvärdera avgången av flyktiga fettsyror (VFA) i matriser av substrat och rötrester vid TS-analys i ugn. Projektet syftade även till att ta fram en metod som för att kompensera för den eventuella förångningen VFA och därmed erhålla ett mer korrekt TS och VS-värde. Inom ramen för projektet utvärderades även förångningen av ammonium och löst

organiskt kol (TOC). Fyra olika substrat och tre olika rötrester analyserades i studien, alla med olika ursprung.

En metod där det torkade TS-provet löstes upp i vatten och därefter analyserades för VFA användes för att utvärdera förångningen av VFA vid ugnstorkning, vid 105°C i 20 timmar. Metoden verifierades genom att höja pH (pH>>pKa) i ett referensprov som innehöll höga koncentrationer av VFA. pH höjdes för att de negativt laddade flyktiga fettsyrorna då skulle interagera med positivt laddade molekyler i materialet och på så sätt inte förångas vid ugnstorkningen. Resultaten från dessa verifieringstester visade att det var möjligt att analysera de organiska fettsyrorna syrorna efter det att det torkade materialet lösts upp i vatten och att metoden var tillförlitlig. Vidare så analyserades även den totala mängden organisk kol i ett referensprov, före respektive efter ugnstorkning, och relaterades till förångningen av VFA. Resultaten visade att 75 % av de lösta organiska föreningar som förångades vid TS-analysen var flyktiga fettsyror som kunde identifieras vid VFA-analysen. Det är alltså ytterst väsentligt att belysa just avgången av VFA vid TS-analysen.

Resultaten från studien visade att förångningen av VFA vid TS-analys i ugn var mellan 95 % och 100 % för de fyra substratet. Då den ursprungliga totala VFA-koncentrationen varierade mellan de olika substraten (3-17 g VFA/L) tyder detta på att den initiala koncentrationen inte påverkar andelen av VFA som förångas vid upphettning av de fyra substraten. Vidare tyder de utförda försöken på att förångningen av VFA var oberoende av molekylvikten för de sju flyktiga fettsyrorna som analyserades (från ättiksyra till heptansyra). Eftersom felen mellan de olika substraten varierade går det inte att generalisera felet i VS-vikten för alla typer av substrat. Det är alltså mycket viktigt att analysera koncentrationen av VFA i sitt material för att få en indikation på hur stort felet är vid varje specifik biogasanläggning eller substratsmix.

I biogödselproverna var resultatet dock annorlunda. Initialkoncentrationerna av VFA var generellt lägre samtidigt som pH-halten var högre. Förångningen i de tre biogödseln var lägre än i de undersökta substraten och varierade mellan 0-55%; med en högre avgång med en ökande koncentration av VFA. En lägre avgång av VFA var också väntad eftersom en större andel av VFA är, teoretiskt sett negativt laddade vid ett högre pH jämfört med vid lägre pH, som t.ex. i de analyserade substraten. I de fyra substraten var även det ursprungliga pH-värde lågt (≤5.2), vilket kan jämföras med pH i biogödseln som var nära 8. Detta tyder på att pH är en viktig parameterar som inverkar på andelen VFA som angår vid TS-analys i ugn.

För de fyra substraten resulterade avgången av VFA vid TS-analysen ett fel på 3-31% av VS-vikten. Felet varierade stort från substrat till substrat beroende på kvoten mellan TS och VFA koncentrationen. Följaktligen, substrat som innehöll höga koncentrationer av VFA och samtidigt hade relativt låg TS-halt resulterade i störst fel på VS-vikten.

Om ingen kompensation för avgång av VFA utförs erhålls en högre organisk belastning än önskat. Detta samtidigt som det finns en risk att den specifika gasproduktionen överskattas. Utan kompensering för förångningen av VFA kan man med det substrat som hade högst VFA-avgång av misstag belasta sin process med organisk belastning som är 31 % högre än önskat. Andra konsekvenser som detta kan ge är att felaktiga slutsatser dras t.ex. om två substrat skall jämföras med varandra, varvid det ena innehåller höga koncentrationer av VFA medan det andra inte gör det. Vidare kan detta ge falska

positiva resultat i s.k. utrötningsförsök som ofta används för att värdera ett substrats metangaspotential. Utrötningsgraden baseras på TS och VS i både ingående substrat och utgående biogödsel vilket innebär att felet i denna parameter till och med kan bli högre jämfört med felen i belastning och specifik gasproduktion. Om både substratet och biogödseln innehåller höga koncentrationer av VFA, vilket kan vara fallet i vissa typer av biogasprocesser, skulle alltså felet kunna bli mycket stort.

Vid utvärdering av förångning observerades även att en stor andel av ammoniuminnehållet avgår vid TS-analys i ugn. Detta kan vara av betydelse för analysen av biogödsel, där koncentrationen av ammonium är hög relativt TS-halten. Vilken betydelse förångningen av ammonium har för analysresultatet för TS- och VS-halten har inte klargjorts i detta projekt utan bör utredas ytterligare.

För att göra resultaten från studien så generella och lätta att använda på en biogasanläggning eller på ett laboratorium som möjligt har två metoder förslagits med olika noggrannhet för att kompensera för avgången av VFA. I båda metoderna behöver man ha kännedom om sina material och innehållet av flyktiga fettsyror som potentiellt skulle kunna avgå. Metod 1, baseras på observationen av att flyktigheten för VFA i sura substrat är >95%. För att utföra kompensationen krävs med denna metod analysvärden för VFA, TS och VS i substratet. Metod 2 innebär att kompensationen genomförs på samma sätt som de material som har undersökts i denna studie, genom att VFA analyseras i både vätskefasen samt i den i vatten upplösta torra fasen efter ugnstorkningen. Genom att sedan beräkna graden flyktighet kan ett kompenserat värde för TS och VS beräknas specifikt för just detta material. Denna metod kan alltså användas både på substrat och biogödsel.

Sammanfattningsvis, visar resultaten från denna studie att det är mycket viktig att beakta förångningen av VFA vid TS-analys i ugn. Det är därför viktigt att kompensera uppmätta TS- och VS-värden för den VFA som avgår vid analysen. Metoderna för att kompensera för förångningen som presenteras i denna rapport är enkla att använda, men det kräver att TS, VS och VFA koncentrationen analyseras på materialen och kontinuerligt följs upp om variationer förekommer i materialen. Genom att kompensera för förångningen av VFA erhålls mer korrekta värden för TS och VS-värden. Detta bidrar till en förbättrad möjlighet att styra och övervaka biogasprocessen liksom en bättre jämförelse av olika driftparametrar mellan olika biogasanläggningar.

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1   Background

The interest for bio-methane as a renewable energy source has increased over the last couple of years. In Sweden, this increasing interest has mainly been due to a growing demand for bio-methane to be used as vehicle fuel. The research publications regarding bio-methane production have also increased over the last couple of years, which shows that there is a large interest for bio-methane as a renewable energy source worldwide (search term "biogas", Web of Science). The production of bio-methane also has other positive effects for our society, besides the possibility to be used for the production of vehicle fuel, heat and electricity. In commercial bio-methane production, where the degradation of organic material takes place under controlled conditions in biogas digesters instead of just putting it in a landfill, the contribution of methane to the atmosphere can be reduced. Another positive aspect is that the digestate formed in the digester can be used as a fertilizer, thus decreasing the demand for mineral fertilizers and enabling a recycling of nutrient between urban and rural areas (Tafdrup, 1995; Ward et al., 2008).

In order to accomplish a more efficient and optimal bio-methane production, more knowledge is still required. One important factor in order to accomplish a stable biogas production is a regular surveillance of the digestion process (Madsen et al., 2011). Changes of operation conditions can have a great impact on the performance of the digestion process. Imbalance in the digester due to poor process follow-up may result in a decrease in the production of biogas or even serious process failures. An imbalance in the digester and a decreased biogas production is often associated with high costs. Reliable control systems are believed to become of great importance for the development and successfulness of the biogas production as an energy source in the future (Lomborg et al., 2009). Knowledge of the characteristics of the substrate and of the digestate is essential for efficient monitoring of the biogas process. With a good characterization of the substrate, parameters such as the organic load to the digester can be optimized and inhibition of the microbial activity can be avoided. Characterization of the digestate is important to determine the nutrient value and the application rate when it is used as a fertilizer. Characterization parameters frequently used in order to control the substrate and the digestate are for example dry-matter content (DM), volatile solids content (VS), concentration of volatile fatty acids (VFAs), pH, alkalinity and concentration of ammonium.

A common method to determine the DM-value is by oven-drying. In Sweden, this is performed according to, or *slightly modified*, to the Swedish Standard method: SS 02 81 13 (SIS, 1981). According to SS 02 81 13 (SIS, 1981), DM for sludge samples and sediment samples, should be dried for 20 hours in 105°C and VS is subsequently determined by drying the sample for 2 hours in 550°C. The oven-drying method is robust and easy to use. However, a problem with this method is the evaporation of other molecules besides water during the drying process, which can result in an underestimation of the DM content (Kreuger et al., 2011; Larsen & Jones, 1973; Porter & Murray, 2001; Samuelsson et al., 2006; Weißbach & Strubelt, 2008a; Weißbach & Strubelt, 2008b). If the DM content is underestimated this in turn results in an underestimation of the VS content and consequently also an underestimation of the organic loading rate (OLR), an overestimation of the specific gas production, an overestimation of the methane yield as well as errors in the calculated degree of degradation. This phenomenon

has been observed and is a well-known problem in the field of animal food production. Volatility coefficients based upon the evaporation of VFAs in different types of silage have been published in the literature (Weißbach & Strubelt, 2008a; Weißbach & Strubelt, 2008b). However, the biogas field has not paid much attention to this problem. This project focuses on oven DM-analysis and errors in the DM content due to the loss of mainly VFAs during the oven-drying of biogas substrates and biogas digestates.

1.1 Aim

The aim of this study was to develop a method that could be used to compensate for errors obtained in the analysis of the DM content due to the loss of VFAs using the oven-drying technique. To achieve this aim, the evaporation of different VFAs during the oven-drying was investigated and volatility constants were calculated based upon the obtained results. Moreover, the study included an investigation of the possibility to correlate the loss of VFAs during the drying to the total amount of dissolved carbons in the investigated samples. In addition to VFA, the loss of ammonia during the DM-analysis was also analyzed and a literature study of different methods to determine the DM content was performed.

This project was designed to answer five questions:

1. Which VFAs are lost from a sample during the DM-analysis?
2. How much of each VFA is lost from the sample during the DM-analysis?
3. Is the evaporation of the VFAs dependent upon the initial concentrations of the VFAs in the samples?
4. Does the evaporation of VFAs differ between different types of materials e.g. digestates and substrates and is there a difference between the same types of materials obtained from different full-scale biogas plants?
5. Is there a correlation between the relative amount of VFAs that is lost during the drying and the total amount of carbon (TOC) present in the material?

1.2 Dry-matter content

The dry-matter (DM) content, also known as the total solids (TS), is a widely used parameter for the characterization of substrates and digestates. The DM content is the amount of sample left in a sample after water has been removed (Figure 1). The DM consists of organic material known as the volatile solids (VS) and inorganic material known as the ash. The VS represent the part of the DM, which can be converted to biogas and is often expressed as a percentage of the DM content.
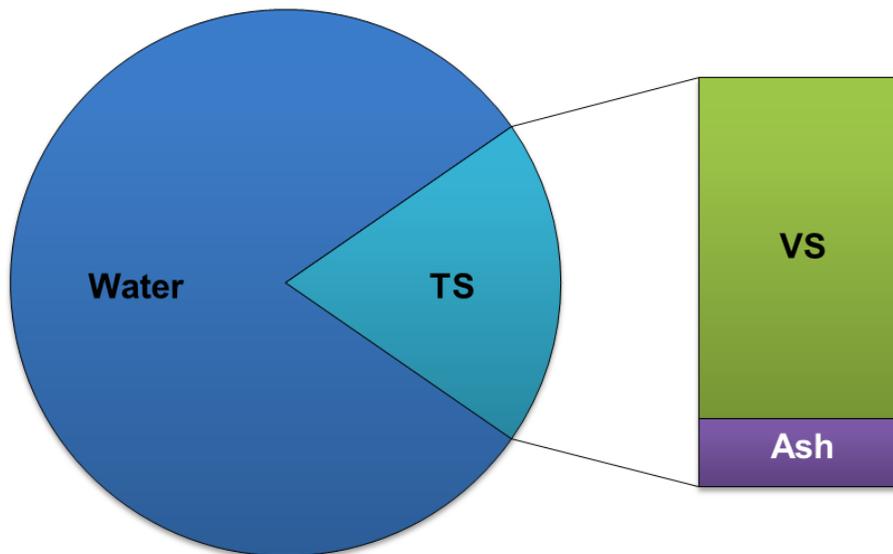
Figure 1. A schematic figure showing the relationship between the dry-matter (DM) content, the volatile solids (VS) content and the ash content.

The measures DM and VS content are used in operation of biogas plants for different purposes. Generally, these measurements can be divided in three main categories:

- Substrate measurements – to monitor the quality of the substrate, organic loading rate and specific biogas production
- Digestion measurements – to monitor the process stability
- Digestate measurements – to evaluate the quality of the bio-fertilizer

Substrates used for biogas production commonly consist of a variety of different types of organic material. Substrates are characterized to get information of the organic content of a specific substrate or a substrate mixture. A substrate mixture typically contains waste products such as household waste, food industry waste, agriculture waste and sludge from wastewater treatment plants. Other common substrates are silage, stillage, glycerin and alcohols (Carlsson & Uldal, 2009). The substrates may contain different amounts of fat, carbohydrate and protein, all with diverse properties but highly degradable in the biogas process. Agriculture waste and wood residuals may also consist of organic material that is non-biodegradable due to high content of lignin.

In biogas production, it is important to monitor and to know the organic loading rate (OLR) to avoid stress on the microorganisms active in the biogas process and secure stable conditions. The organic content of the substrate and the substrate mixture must be quantified, to be able to calculate the organic load. It is important not to judge the DM content based on the viscosity of *a* substance. The DM of for example milk and cream are approximately 10% and 60%, respectively. In spite of this difference, we experience these products as relatively equally "wet", which in a biogas context can have devastating consequences as it is the "dry" component that is converted to biogas, and not the water.

Digestion measures are parameters that are used for process monitoring and these parameters are relaying on DM and VS values. These measures are monitoring the effectiveness of the anaerobic degradation. Examples of

parameters in this category are the specific gas production (Nm^3 kg^{-1}), the organic loading rate (kg VS m^{-3} d^{-1}) and the degree of degradation (%). By following these parameters regularly in daily operation, the process can be closely monitored, which is important to enable a stable biogas production. These measures can also be used for benchmarking the production against other plants and historic data of the biogas plant in operation.

Chemical analyzes are performed on the digestate (also named bio fertilizer). Several plants in Sweden have their bio-fertilizer certified according to SPCR 120 (SP, 2010). These certification rules specify conditions of certification, technical standards and requirements for continuous monitoring of certified bio-fertilizer. Most of the analyzed parameters are expressed as a function of the DM content (SP, 2010).

1.3 Methods to determine the dry-matter content

A number of different methods have been developed to determine the dry-matter (DM) content of various samples. The most frequently used method in Sweden, for biogas applications, is an oven-drying technique. Other methods that can be used to determine the DM content are e.g. the Karl Fisher titration (Petit et al. 1997; Porter and Barton 1997), microwave oven-drying (Marquez et al., 1995), infrared drying near infrared reflection spectroscopy (NIR-spectroscopy) (Lomborg et al. 2009), freeze drying (Samuelsson et al. 2006), distillation (Samuelsson et al. 2006) and acoustic chemometrics (Lomborg et al. 2009).

1.3.1 *Oven-drying methods*

The oven-drying method can be used to determine the dry-matter (DM) content in various materials. A known amount of a sample is dried in an oven at a set temperature and for a specific time-period. Water evaporates from the sample during the drying and the relative amount of DM can be calculated by comparing the weight of the sample before and after the drying.

Several different oven-drying methods are used worldwide. In Sweden, drying techniques, that are based upon the accredited Swedish Standard method SS 02 81 13:1981-05-20 (SIS, 1981), are most frequently used in laboratories performing analysis on sludge and sediments. According to this standard, the sample should be dried in an oven at 105°C for 20 hours. However, if the same standard is applied on waste waters, the drying time is only required to be 2 hours (SIS, 1981). According to another oven-drying methods, the samples should first be dried to a constant weight at a temperature of approximately 60-65°C and then dried at 105°C for three hours (Weißbach & Strubelt, 2008a) or the DM content can be determined by just drying the samples until their weight is constant (Samuelsson et al., 2006). Other drying temperatures that are used are in the range of 60-130°C (Porter & Murray, 2001; Samuelsson et al., 2006). Moreover, when determining the water content of yoghurt in Germany, the product should be dried at a temperature of 102°C but in Switzerland it is enough if the yoghurt is dried at 87°C (Isengard & Walter, 1998). Also the weight of the samples that are analyzed may differ (Isengard & Walter, 1998). Due to the fact that so many different oven-drying methods exist, with different temperatures, sample weight and drying times, it is difficult to compare the results and draw conclusions concerning the optimal methodology.

A problem with the oven-drying method, in general, is that other volatile molecules besides water may be lost during the analysis. This can potentially result in an underestimation of the DM content of the analyzed material and subsequently also in the VS content (Kreuger et al., 2011; Larsen & Jones, 1973; Porter & Murray, 2001; Samuelsson et al., 2006; Weißbach & Strubelt, 2008a; Weißbach & Strubelt, 2008b). There might also a risk that side reactions or degradation of the substances in the samples are initiated by the heating.

However, the oven-drying technique has also many advantages, which is the reason why this method often is preferred for the analysis of the DM content. The main advantages with oven-drying are that the technique is very simple, robust and straightforward. Furthermore, the technique does not require any advanced nor sophisticated equipment. Consequently, a low-cost instrument with low operating costs can be used. A number of samples can also be analyzed at the same time. Furthermore, by applying oven-drying, the content of volatile solids (VS) can easily be measured by first determining the DM content and thereafter, with the same sample, determine the VS content in an oven at 550°C. The DM determination with oven-drying is in many ways suitable for substrates and digestate from biogas plants. However, it is clear that improvements giving better control of the loss of volatile organic compounds are necessary.

1.3.2 *Microwave oven-drying*

The motivation for the development of microwave oven-drying techniques was to shorten the measurement time compared to the oven-drying methods (Isengard & Walter, 1998). The risk of introducing side reactions is also reduced when shortening the drying time (Reh & Gerber, 2003).

When using the microwave oven-drying technique, one can choose to dry the sample during a certain time or to dry the sample until the weight is constant, as when using the oven-drying technique. The results might vary when drying different amounts of the samples during a certain time. Consequently, it is better to dry the samples until the weight of the sample is constant (Isengard & Walter, 1998). If the materials contains molecules that absorbs light in the microwave region, care needs to be taken to avoid overheating of the materials (Reh & Gerber, 2003). The technique is very straightforward and the measurement time as well as the analysis time is fast. The measurement with microwave technique applied on dairy products is fast with a time of analysis of less than 5 min (Reh & Gerber, 2003). According to our knowledge it is not common to use microwave oven-drying to analyze the DM content in samples used in the biogas production.

1.3.3 *Infrared drying*

The infrared (IR) drying method to determine the DM content is a quick and commonly used at full scale biogas plants. The sample is dried with IR radiation at a certain temperature during a specific time, e.g. at 120°C for 20 minutes. The measurement time is thus shorter than the oven-drying, but it is normally only possible to analyze one sample at the time. The DM content is calculated by comparing the weight of the samples before and after the drying, as for the oven- and microwave-drying. Commercially available instruments for infrared drying exists that are very simple to use. When a material is heated there is always a risk that other molecules besides water, such as the VFAs, are lost during the analysis.

A higher value of the DM is often observed when comparing values obtained from infrared drying with DM values from oven-drying for the same sample. This could be due to e.g. that the loss of VFAs is lower and that not all of the water has been removed from the samples.

1.3.4 *Karl-Fischer titration*

The Karl-Fisher (KF) titration method was developed in the mid-1930th and it is a frequently used method to determine the DM content in for example food (De Caro et al., 2001; MacLeod, 1991). The method is based on the highly selective reaction between water (H_2O) and iodine (I_2) and can be used to detect very low concentrations of water. The detection can be either colorimetric or volumetric. The water in the samples needs to be unbound to be able to react with iodine and therefore the samples need to be processed before the analysis. The preparation of the samples can take between 1-2 hours depending on the sample type but the actual measurement is fast (1-2 minutes). Alternative preparation methods to decrease the time before the measurement have been presented in the literature (De Caro et al., 2001).

A problem with the KF titration method is that side reactions, between the materials to be analyzed and the chemicals used in the titration, are possible (MacLeod, 1991). These reactions can cause errors in the results, resulting in an underestimation or overestimation of the water content in the analyzed material (MacLeod, 1991). From the analysis of the results it can be very complicated to separate a KF titration involving side reactions from a normal KF titration.

One other complication when using KF titration method is that iodine can be oxidized by for example Fe^{3+}, Cu^{2+} and NO_2^- (MacLeod, 1991). As a result, the water content will be underestimated since the oxidized iodine cannot react with water present in the sample. The water content can also be underestimated if the analyzed materials contain sulfur dioxide and molecules, which contain a carbonyl functional group e.g. aldehydes or ketones, since these can form complexes with water (MacLeod, 1991). As the materials used for anaerobic digestion often contains a very large variety of molecules and substances it seems reasonable to assume that the Karl-Fischer method to determine the water content in these materials might be complicated. However, this still needs to be investigated.

1.3.5 *Near infrared spectroscopy*

Near infrared spectroscopy (NIR) has been suggested as a potential technique to be used for online monitoring on full scale plants and the method has e.g. been used to measure the DM content (Lomborg et al., 2009), the VS content (Nordberg et al., 2010) and the amount of VFAs (Lomborg et al., 2009) in substrates. The materials are irradiated with electromagnetic radiation and quantitative information regarding e.g. the DM content can be obtained by analyzing how much of the electromagnetic radiation that is absorbed, transmitted or reflected by the material (Lomborg et al., 2009; Nicolaïa et al., 2007). For NIR, electromagnetic radiation with a wavelength between 780-2500 nm is being used (Nicolaïa et al., 2007).

1.4   Anaerobic digestion

1.4.1   *Process biology*

In order to degrade organic material to methane and carbon dioxide in a biogas process a close cooperation between different microorganisms, with different metabolic capacities, is required (Gerardi, 2003). Many organisms are also so called syntrophs, i.e. they benefit from the activity of each other and successfully break down organic matter (substrate) that neither one could manage alone. During the formation of biogas, complex polymers and structures are hydrolyzed to simple monomers, in the first step (Figure 2). Fat is for example converted to fatty acids and glycerol, proteins into amino acids, and cellulose and starch into glucose. The produced monomers are taken up by the bacteria in the next step, called the 'fermentative step' or the acidogenesis. During this step, monomers are converted into smaller compounds such as ethanol, lactic acid and volatile fatty acids (VFAs), such as acetic acid, propionic acid, butyric acid. In addition, hydrogen gas (H_2) and carbon dioxide (CO_2) are also formed (Gerardi, 2003). The produced VFAs are further converted to acetic acid, hydrogen gas and carbon dioxide, provided that the hydrogen is kept at a low pressure by a rapidly consumption by hydrogenotrophic (hydrogen-consuming) methane formers. Acetic acid, hydrogen gas (H_2) and carbon dioxide (CO_2) form the primary substrates for acetoclastic (acetic acid-consuming) and hydrogenotrophic methane formers, respectively (Gerardi, 2003). The methane-forming step is generally considered to be rate-limiting in the biogas process but the hydrolysis step can also be the bottle neck in the degradation, depending on the character of the substrates. This means that the rate of the hydrolysis step might for some substrates, e.g. cellulose or other polymeric materials, be slower than the methane-forming step.

At least three co-operating organism populations are required to achieve complete degradation of organic matter to methane and carbon dioxide. However, in a properly functioning biogas process, there are often many more due to the complexity of the ingoing material.
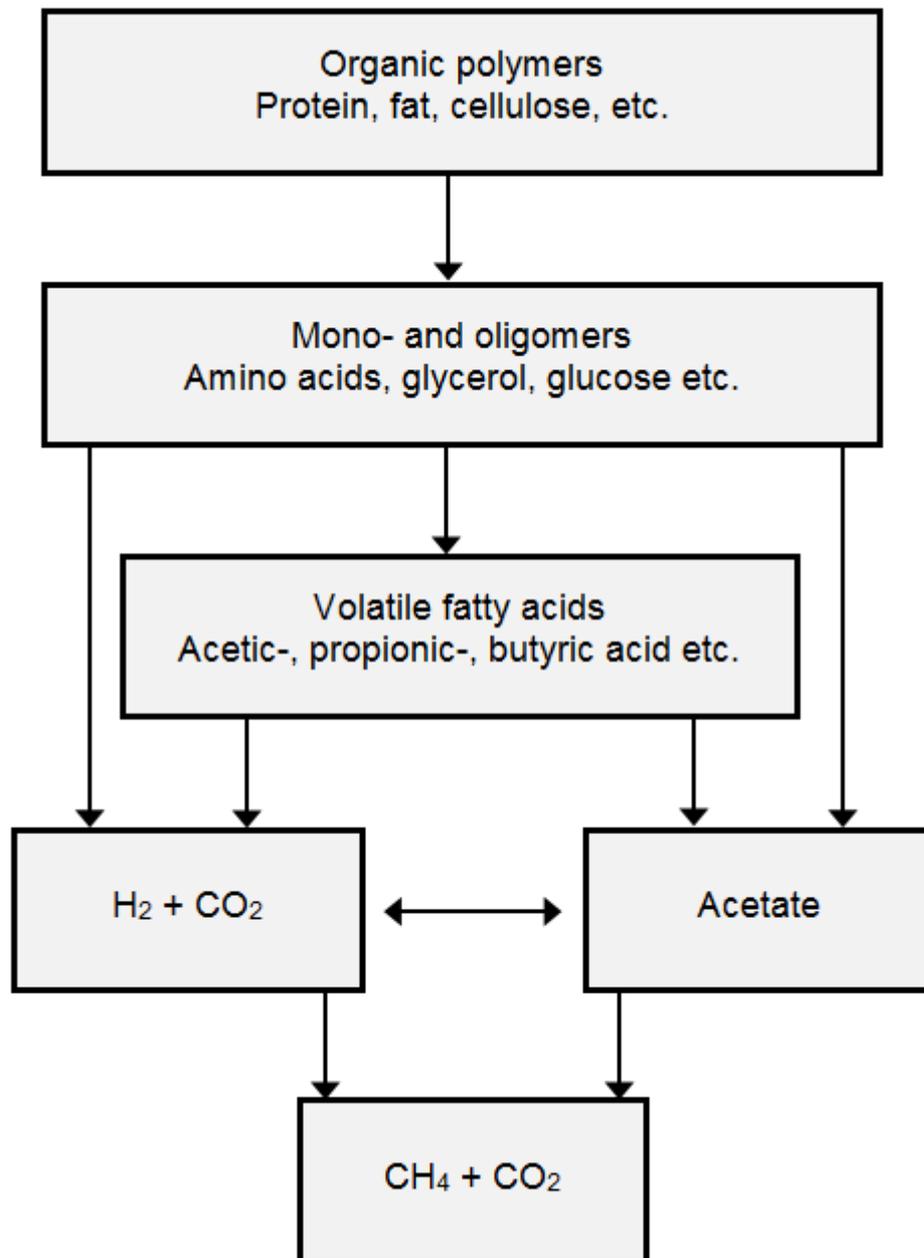
Figure 2. Degradation of organic matter to methane and carbon dioxide under anaerobic conditions.

1.4.2 Process instability

It is important for the degradation process that the biological system is balanced and that the cooperation between the different groups of bacteria is effective. If too much volatile solids continuously are fed into the reactor, and the microorganisms are unable to consume all VFAs formed, an increase in acetate and hydrogen gas ensues. High concentrations of hydrogen gas and acetate may lead to further imbalance in the degradation process and as a consequence various VFAs may start to accumulate (Ahring et al., 1995). If the process instability is driven further, this will result in a decrease in alkalinity, finally resulting in a decrease in pH. When pH decreases a larger amount of the VFAs become uncharged and more

repellant of water. If this situation is allowed to continue, there is a high risk for foaming (Ganidi et al., 2009).

1.5 Process parameters

There are several biogas process parameters of importance for operation and surveillance of biogas digester, including DM and VS content. Many of these parameters are used both in research and full scale operation. The main parameters depending on DM and VS are further explained, in this section.

1.5.1 *Maximum bio-methane potential*

A common way to determine the potential of a certain substrate is to perform a bio-methane potential test. This type of test is normally performed in lab-scale batch conditions and gives information of the potential methane production of the substrate. For a full-scale production plant, this test is for example of interest during an evaluation concerning the possible economical profit to treat a specific substrate. In this test, the DM and VS value of the substrate is of critical importance as the methane production from the investigated substrate is related to the VS content. Thus, a correct DM and VS measurement is essential. If the DM or VS is underestimated, due to loss of VFA or other organic compounds, the maximum bio-methane potential may be overestimated which can lead to wrong decisions at a full-scale plant or wrong conclusions in scientific reports.

1.5.2 *Specific gas production*

The specific gas production provides information about the gas potential of the added substrates to the digestion process. When treating a constant and similar substrate mixture (inlet feed) each day, a stable and equal specific gas production is expected. Even if the inlet-flow to the digesters varies, the specific gas production should be similar from one day to another due to the normalization to the organic loading rate (Equation 1). Change in the specific gas production that cannot be related to change of substrate or dramatic change in OLR can indicate that the process is undergoing a process disturbance.

Equation 1)

$$\frac{Gas\ Flow}{DM_{substrate} * VS_{substrate} * Volume_{substrate}} * \left(\frac{Nm^3\ gas}{kg\ VS}\right)$$

Also here a correct VS value is essential. An underestimation of the VS will result in an overestimation in the specific gas production. This overestimation possesses a problem when e.g. evaluating the biogas potential of different substrates, potentially resulting in wrong decision regarding the priorities of the substrate of interest. Variations in analysis results for DM and VS due to differences in the concentration of volatile substances within the substrate will also result in incorrect conclusion that the calculated specific gas production is varying.

1.5.3 *Organic loading rate (OLR)*

OLR is a parameter which gives information about the amount of organic material that is being fed to the digester, with a specific volume. OLR can easily be calculated (Equation 2) if the flow, DM and VS of the substrate are known.

Equation 2)

$$\frac{Volume_{substrate} * DM_{substrate} * VS_{substrate}}{Volume_{digester} * d} * \left(\frac{kg\ VS}{m^3 * d}\right)$$

When performing wet anaerobic digestion at mesophilic temperatures ($\sim 37^{\circ}$C), typical values for the OLR are 2-4 kg VS m^{-3} d^{-1} (Ek et al., 2011; Nordell et al., 2013). In a thermophilic process these values are slightly higher. The optimal condition for the microorganisms is to maintain an OLR as stable as possible. Overloading a digesters and having a rapidly fluctuating OLR may lead to accumulation of VFAs, which in turn can cause a decrease in pH and consequently a decrease in gas yield due to stressed microorganisms. Conclusively it is important to secure a stable and not to high OLR. Thus, underestimation of DM and VS may cause severe problems as this my mistake could results in an overload, giving unfavorable conditions for the microorganism present in the digester.

1.5.4 *Degree of degradation*

Degree of degradation is a parameter used for evaluation of the process efficiency. This parameter does not take into account the biogas potential of the added substrate. Instead the degree of the degradation is a parameter that describes the amount of added organic material that actually has been converted into biogas under the prevailing conditions. A high value of the degree of degradation indicates a well performing digestion process and an easily degradable substrate. Calculations can be performed according to equation 3. Due to the restrictions of the CSTR-system (continuous in- and outtake) and energy need for the microorganism's growth, the degree of degradation normally do not exceed 80%. During the calculation both DM and VS content of the substrate as well as of the digestate are used. Consequently using false low values of DM and VS may result in large errors.

The degree of degradation will be overestimated if the VS of the digestate is underestimated. As a consequence, wrong conclusions concerning the process performance could be made, i.e. one could think the process is still working properly since the degree of degradation is high despite the fact that the digestate contains a lot of VFAs. This could then lead to wrong decision concerning the priority when choosing between different substrate to be used in the biogas production. The degree of degradation will be overestimated if the VS of the digestate is underestimated. This could contribute to mistakes due to the fact that one would think the process is still working properly since the degree of degradation is high despite the fact that the digestate contains a lot of VFAs.

Equation 3)

$$\left(1 - \frac{DM_{digestate} * VS_{digestate}}{DM_{substrate} * VS_{substrate}}\right) * 100 \ (\%)$$

1.6   Volatility

The volatility of molecules is dependent both on the chemical properties of the molecules themselves and upon the surrounding environment. Volatile molecules have a high so-called vapor pressure at a certain temperature compared to other molecules (Ebbing, 1993). An example of a very volatile molecule is chloroform, which has a vapor pressure of 160 mmHg at a temperature of 20°C (www.sigmaaldrich.com). This can be compared to ethanol and water, which have vapor pressures of 44.6 and 17.3 mmHg, respectively at the same temperature (20°C) (Table 1). Normally, the vapor pressure decreases with the molecular weight when comparing molecules with similar molecular structure. This can be observed for the VFAs that have been investigated in this study (Table 1). The lowest vapor pressure is found for heptanoic acid (<0.1 mmHg) and the highest is found for acetic acid (11.4 mmHg). Consequently, acetic acid is, when just considering the vapor pressure, more volatile than heptanoic acid. In order for a molecular transition to occur from the liquid phase to the gas phase (vaporization), the kinetic energy of the molecules in the liquid must become higher than their potential energy (Ebbing, 1993), which is determined by e.g. intermolecular interactions such as electrostatic interactions or hydrogen bonding. This means that if molecules in a liquid are charged, thus interacting with other charged molecules, the volatility decreases.

1.6.1   *The chemistry of volatile fatty acids (VFA)*

The intermediary products from the acidogenesis are volatile compounds such as organic acids and alcohols. Alcohols such as methanol and ethanol have a much higher vapor pressure and lower boiling points compared to the VFAs (Table 1). Methanol and ethanol have boiling points below 100°C, while all the VFAs have boiling points above 100°C (Table 1).

Table 1. The properties of different volatile compounds such as volatile fatty acids and alcohols.

Compounds	Formula	pKa[1]	Mol weigth[1] (g/mol)	TOC (%)	Boiling point (^{o}C)	Vapor pressure (mm Hg)**
Formic acid	CH_2O_2	3,75	46,0	26%	101[1]	
Acetic acid	$C_2H_4O_2$	4,75	60,0	40%	118[1]	11,4[2]
Propionic acid	$C_3H_6O_2$	4,87	74,0	49%	141[1]	2,4[2]
Lactic acid	$C_3H_6O_3$	3,86	90,1	40%	122	
Butyric acid	$C_4H_7O_2$	4,82	88,1	54%	163[1]	0,43[2]
Iso-butyric acid	$C_4H_8O_2$	4,86	88,1	54%	155[1]	1,5[2]
Valeric acid	$C_5H_{10}O_2$	4,82	102,1	59%	186[1]	0,15[2]
Iso-Valeric acid	$C_5H_{10}O_2$	4,78	102,1	59%	176	0,38[2]
Hexanoic acid	$C_6H_{12}O_2$	4,88	116,1	62%	206[1]	0,18[2]
Iso-hexanoic acid	$C_6H_{12}O_2$	4,85	116,1	62%		
Heptanoic acid	$C_7H_{14}O_2$	4,71	130,1	65%	223	<0,1[2]
Methanol	CH_4OH	-	32,0	36%	65	97,7[2]
Ethanol	C_2H_5OH	-	46,1	52%	78	44,6[2]
Propanol	C_3H_7OH	-	60,1	60%	97	33[2]

* Theoretical
** At 20 °C
[1] SI-data
[2] sigma-aldrich

Charged VFAs will interact with other charged molecules/substances in the materials. Consequently, these VFAs will have a lower volatility compared to uncharged VFAs. The degree of ionization is determined by the pH of the material and majority of the VFAs will be uncharged if the pH<<pKa (Figure 3).
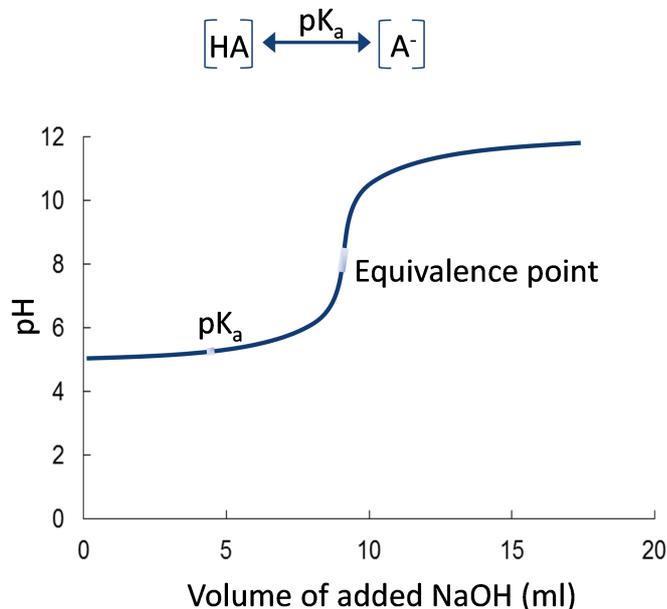

Figure 3. A typical titration curve for a buffered system such as a biogas substrate with a low pH to which a base is added. At the pKa, the amount of ionized and unionized acids is equal for a certain acid.

1.6.2 *VFA content in the substrate*

Even though a substrate, originally, normally consists of fat, protein and carbohydrates, this may not be the fact when the substrates enter the digestion process. With easy available substrates such as food waste and slaughterhouse waste, the degradation often starts already when the substrates are held in stock in e.g. storage tanks at the biogas plant. The biological activity may be particularly high during the summer when the temperature is high. This biological process does typically not include methanogenesis but the substrates may undergo the first steps in the anaerobic process: the hydrolysis and the acidogenesis. This may lead to an early start of the anaerobic process and formation of multiple organic compounds such as alcohols and volatile fatty acids, which can contribute to a very low pH of the substrate. The low pH is an unsuitable condition for methanogenesis to occur, and therefore the VFA is still within the substrate when it finally enters the digester. The VFA concentration in a substrate mixture can thus sometimes represent a large share of the DM and the VS content, which make it important to ensure that a reliable method for DM and VS measurement is applied to avoid an underestimate of the VS content.

2 Experimental

Seven materials were investigated in this study. The study included three different substrates from full scale biogas plants in Sweden: two pasteurized food and slaughterhouse mixtures, abbreviated S1 and S2, as well as one grass silage material, abbreviated S3. The study also included sludge from grease separators, to be treated at a water treatment plant in Sweden, abbreviated S4. Besides the four substrates, the study also included three digestates, abbreviated D1, D2 and D3. The digestates D1 and D2 originated from two different full scale plants in Sweden. The digestate D3 originated from a bio-reactor used in a lab-scale experiment.

2.1 General analysis procedure

The concentrations of DM, VFA, pH, ammonium and TOC were all determined with the same analysis procedure for all samples.

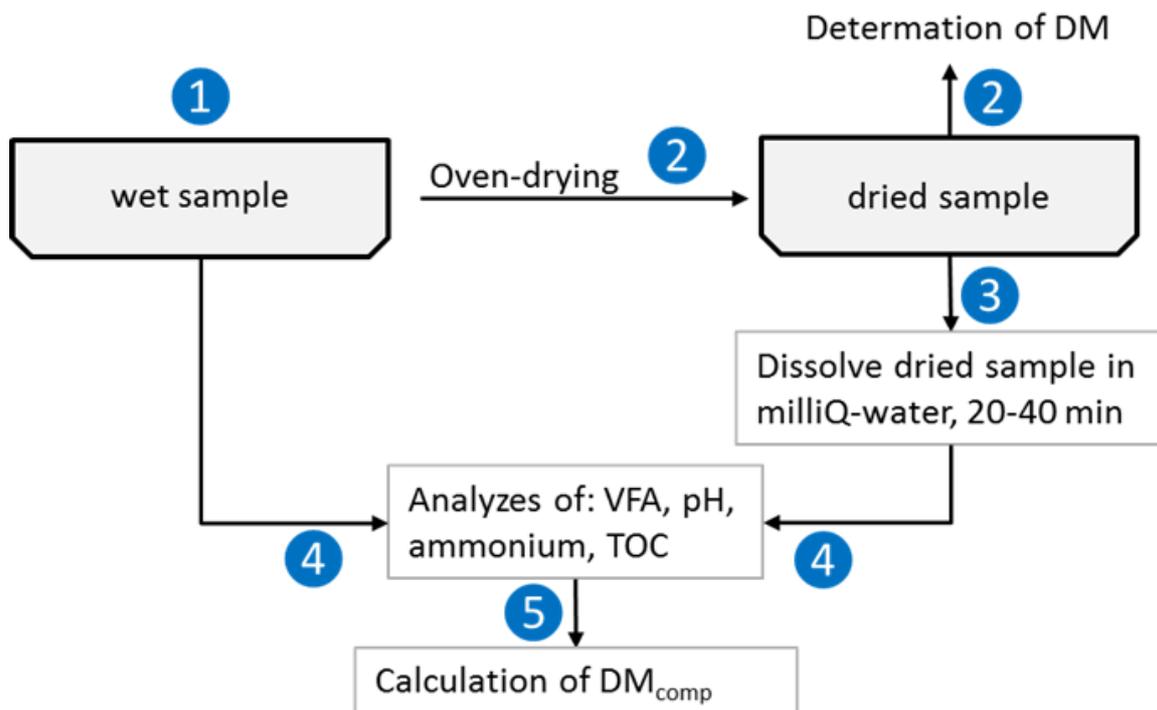*Figure 4. A sketch of the analysis procedures used in the project.*

1) A known weight of the wet material was placed in the DM-oven.

2) The DM content was determined according to the description in Chapter 2.3 (Analysis methods and calculations)

3) A known amount of MilliQ water (≈9-20 g depending on the sample) was allowed to soak into the dried sample for 5-10 minutes and the obtained

solution (dissolved dried sample + MilliQ water) was then stirred for 15-30 minutes.

4) The VFA concentration, the pH or the dissolved TOC in the original sample as well as the soaked dissolved dried sample were analyzed according to the description in Chapter 2.3. For the ammonium analysis, the dried material was investigated according to the procedure described in Chapter 2.3 (Analysis methods and calculations).

5) Calculations were performed to determine the VFA compensated DM-value (DM_{comp}, Equation 7), i.e. the amount of acids that evaporated during the drying (difference between VFA content in the wet and dried sample) were added to the DM value.

2.2 Validation of the general analysis procedure

To verify that it was possible to analyze VFA in dried samples, which had been dissolved in MilliQ water, the pH was increased in test samples (pH>11) before the DM analysis using oven-drying. The modification of pH was performed by adding approximately 30 ml of 1M NaOH to about 100 ml of substrate S1 ($S1_{NaOH}$) and by adding 29 ml of 1M NaOH to 107 ml of the substrate S2 ($S2_{NaOH}$). The concentration of VFA in the wet sample was compared to the concentration of the VFA in the dissolved dried sample.

2.3 Analysis methods and calculations

The DM was analyzed by drying a known weight (~10 g) of the wet sample (wet weight) according to SS 02 81 13 (SIS, 1981); in an oven for 20 hours at 105 °C. The samples were then placed in a desiccator, to avoid accumulation of water, until the samples had cool down and the weight of the material was thereafter measured (DM weight).

To determine the VS, the dried material was further heated at 550 °C for 3 hours, which is slightly modified compared to the SS 02 81 13 (SIS, 1981) where 2 hours which is stated. The material was then allowed to cool down in a desiccator before the weight of the material was measured (ash weight). The DM and VS were analyzed in at least six independent samples for each of the investigated materials. The DM (%) and VS (% of DM) were calculated according to equations 4 and 5, respectively. The VFA concentration within the dried sample was calculated according to equation 6 and the volatility according to equation 7.

Equation 4)

$$\left(\frac{DM\ weight}{Wet\ weight}\right) * 100 = Dry\ matter\ content\ (\%)$$

Equation 5)

$$\left(1 - \left(\frac{Ash\ weight}{DM\ weight}\right)\right) * 100 = VS\ (\%\ of\ TS)$$

Equation 6)

$$VFA_{dried,sample}\ (mg/L) = VFA_{dissolved,dried} * \left(\frac{(m_{sample,dried} + m_{water})}{m_{sample,initial}}\right)(mg/L)$$

Equation 7)

$$VFA_{volatility}\ (\%) = \left(1 - \frac{VFA_{dried,sample}(mg/L)}{VFA_{wet,sample}(mg/L)}\right) * 100$$

The VFA compensated DM_{comp} and VS_{comp} were calculated according to the Equations 8 and 9, where DM_m is the measured DM value, VS_m is the measured VS value and $VFA_{volatility}$ is the volatility of the VFA based upon the total concentration of VFA.

Equation 8)

$$DM_{comp}\ (\%) = DM_m(\%) + \left(\frac{VFA_{volatility}\ (\%)}{100} * VFA_{initial}(mg/L)\right) * 10^{-4}$$

Equation 9)

$$VS_{comp}\ (\%\ of\ DM_{comp})$$
$$= \frac{\left(DM_m(\%) * VS_m\ (\%)\right) + (10^{-4} * VFA_{vol}\ (\%) * VFA_m(mg/L))}{DM_{comp}(\%)}$$

The VFAs were analyzed using a Clarus 550 gas chromatograph (Perkin Elmer, USA) equipped with a packed Elite-FFAP column used for acidic compounds (Jonsson & Borén, 2002). The VFA was analyzed in at least three independent wet samples and three independent dissolved dried samples for each of the investigated materials and the presented values are the average of the three measurements. The presented VFAs concentrations for the dissolved dried samples have been correlated for the dilution with MilliQ water. The average of the concentration is presented with a 95% confidence interval.

The ammonium (NH_4-N) was analyzed according to the FOSS Tecators application sub note 3502 using a Kjeltec 8200 distillation system (FOSS in Scandinavia, Sweden). The ammonium was analyzed in at least three independent wet samples and three independent dissolved dried samples for all the materials. The presented concentration is the average of the three independent measurements with a 95% confidence interval. The presented concentrations of NH_4-N have been correlated for the dilution. It should be notified

that the concentration of ammonium includes both the ammonium in the NH_4-N state as well as the NH_3-N state.

The TOC was determined in the dissolved fraction of the S1 substrate by centrifugation of the substrate (11 000 rpm, 20 min) and thereafter filtration of the supernatant trough 0.45 µm Millipore filter, TOC was then determined in the filtrate. TOC was analyzed with the instrument Multi N/C 3100 (AnalytikJena UK, United Kingdom) according to the guidelines in SS-EN 1484. Here, the organic carbon in the sample is oxidized to carbon dioxide, using a patina catalyzer and the carbon dioxide concentration is then determined by a NDIR detector. Three independent analyzes were performed on the wet sample and the dissolved dried sample of S1. The pH was measured using a potentiometric pH-meter (WTW Inolab, USA), equipped with a Hamilton electrode, at ≈25°C.

2.4 Sample preparation

The materials S1, S2, D1, D2 and D3 were stored in a freezer at -20 °C until use. The substrates S3 and S4 were placed in a refrigerator at +4 °C and analyzed very shortly after the materials had been received at Tekniska verken. The silage substrate (S3) was diluted in water (S3: Water, 1:5.3) and mixed with a hand blender prior to the analysis of VFAs, pH and ammonium. DM and VS were measured on undiluted material of S3 as described in Chapter 2.3.

3   Results and discussion

The main focus of this project was the evaporation of VFAs, from different materials used in the biogas production, during the DM-analysis by oven-drying. The results from the analyzed substrates and digestates are presented and discussed with respect to the volatility of VFA and the potential errors in DM, VS and different important biogas parameters. The result from evaporation analyzes of ammonium and the total organic carbon are also shown and discussed. Furthermore, two different methods to be used to compensate for errors in DM and VS, due to the loss of VFA, are proposed.

3.1   Samples characterization

Seven different materials were analyzed in this project: two pasteurized mixtures of substrates (S1 and S2), one grass silage (S3), one sludge material from grease separators (S4) and three different digestates (D1, D2 and D3). The characteristics of the seven analyzed materials can be found in Table 2.

Table 2. The characteristics of the materials included in this study.

Sample	DM (%)	VS (% of DM)	VFA (mg/L)	NH_4-N (mg/kg)	pH
S1	7.2 ± 0.2	75 ± 2.0	17 000 ± 570	1 370 ± 39	5.2 ± 0.0
S2	14 ± 0.5	91 ± 0.4	4 300 ± 61	514 ± 142	5.0 ± 0.0
S3	23 ± 0.4	91 ± 0.1	6 500 ± 4	453 ± 206	4.1 ± 0.0
S4	3.6 ± 0.2	99 ± 1.1	3 000 ± 20	48 ± 5	4.6 ± 0.0
D1	3.4 ± 0.0	56 ± 0.2	320 ± 13	2 880 ± 117	7.9 ± 0.1
D2	4.7 ± 0.1	73 ± 0.2	460 ± 33	2 810 ± 65	7.9 ± 0.0
D3	4.2 ± 0.2	76 ± 1.0	7 700 ± 200	5 340 ± 106	8.0 ± 0.0

3.2   Validation of the general analysis procedure

The same general analysis procedure was used in this project to measure the concentration of VFAs in the dried samples. This analysis procedure is described in Chapter 2.1. The samples were first dried and then dissolved in MilliQ water prior to the analysis. To verify this procedure, the pH of substrates S1 and S2 was increased to above 11 before the oven-drying. The S1 and S2 samples to which the NaOH was added are hereafter abbreviated $S1_{NaOH}$ and $S2_{NaOH}$. The aim with this modification of pH was to increase the degree of ionization of the VFAs in the samples. The negatively charged VFAs may interact with positively charged molecules and remain in the sample during the drying and the evaporation should be minimized. Consequently, the concentration of VFAs in the wet and dissolved dried samples should be about the same if the method to analyze VFA in dry materials dissolved in MilliQ is working. The observed results for the pasteurized mixture of materials, $S1_{NaOH}$ and $S2_{NaOH}$ are presented in Tables 3 and 4, respectively.

Table 3. The concentrations of VFAs in the wet and the dissolved dried samples of S1$_{NaOH}$ (pH>11) and the calculated volatility. The volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	6 000	6 100	0
Propionic acid	2 300	2 100	9
Butyric acid	1 300	1 100	15
Iso-butyric acid	300	200	33
Pentanoic acid	930	970	0
Iso-pentanoic acid	300	250	17
Hexanoic acid	1 600	1 700	0
Iso-hexanoic acid	100	80	20
Heptanoic acid	300	250	17
Sum VFA (mg/L)	13 000	12 800	2

The volatility when considering the total concentration of VFAs was calculated to be 2 and 20% for S1$_{NaOH}$ and S2$_{NaOH}$, respectively. These results are in agreement with a previous published article by (Derikx et al., 1994). According to this study, VFAs can be fixed in manures during oven-drying when the pH is above 10. The observed results showed that a majority of the VFAs was detected in both S1$_{NaOH}$ and S2$_{NaOH}$, thus indicating that the method of analyze VFA within a dried samples works.

Table 4. The concentration of VFAs in the wet and the dissolved dried samples of S2$_{NaOH}$ (pH>11) and the calculated volatility (%).The volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	3 000	2 800	7
Propionic acid	660	400	39
Butyric acid	500	280	44
Iso-butyric acid	70	30	57
Pentanoic acid	260	140	46
Iso-pentanoic acid	100	70	30
Hexanoic acid	160	120	25
Iso-hexanoic acid	30	20	33
Heptanoic acid	100	70	30
Sum VFA (mg/L)	4 900	3 900	20

3.3 Evaporation of VFA compared to TOC

The dissolved fraction of total organic carbons (TOC) was analyzed in the substrate with the highest VFA concentration, substrate S1, before oven-drying as well as after oven-drying. By analyzing both VFA and dissolved TOC, the mass-balance of organic carbon within the samples was calculated. Only the dissolved fraction of the samples was analyzed, assuming that no TOC was transferred from solid to dissolved TOC during the oven-drying procedure. During the oven-drying, the dissolved TOC decreased from approximately 16 700 mg/L down to about 6

100 mg/L, while the VFA level decreased from approximately 17 000 mg/L to 780 mg/L (Table 5). The concentration of VFAs in the wet sample corresponded theoretically to about 8 300 mg TOC/L whereas the concentration of VFA in the dissolved dried sample corresponded to approximately 360 mg TOC/L. It should be notified that since the theoretical value of TOC in each VFA differ; calculations of each individual VFA were performed for these calculated TOC values.

Table 5. VFA and TOC within the wet and dissolved dried samples.

Parameter	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Evaporation (mg/L)
VFA	17 000 ± 570	780 ± 140	16 220
Calculated TOC as VFA*	8 300	360	7 940
Measured dissolved TOC	16 700 ± 650	6 100 ± 220	10 600

* Evaporation based on theoretical calculations. No standard division is given.

The evaporated part of TOC, expressed as the difference between wet and dissolved dried sample, corresponded to approximately 10 600 mg TOC/L. However, the amount of evaporated TOC as VFA (data analysis) was only about 8 000 mg TOC/L, corresponding to about 75% of the evaporated TOC during the drying (Figure 5 Subsequently, this indicates that approximately 25% of the evaporated volatile substances were not detected in the VFA analysis. As the TOC method only gives value of organic carbon, this fraction represents unknown volatile organic compounds. However, there are some VFAs that are not detected in the used VFA analysis, such as formic acid (boiling point of ≈101 °C) and lactic acid (boiling point of ≈122 °C). Other common organic compounds that also are volatile and might be present in different types of substrate mixtures are e.g. methanol, ethanol and acetone. However, as illustrated in Figure 5, 75% of the evaporated volatile organic compounds can be detected in VFA-analysis, which shows that a VFA-compensation method is relevant and could result in a reasonable good approximation of the DM and VS values.
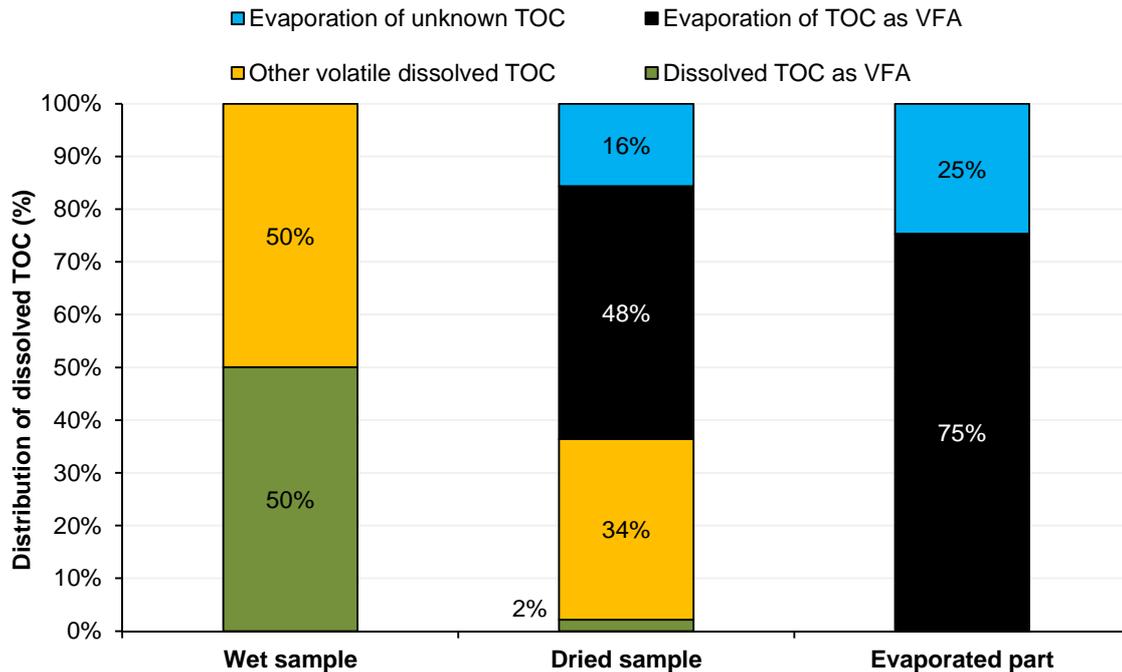
Figure 5. Distribution of volatile dissolved TOC within the wet sample before drying and in the dried sample after oven-drying.

3.4 Volatility of volatile fatty acids (VFA)

3.4.1 *Substrate S1*

As can be seen in Table 6, the analysis of the degree of evaporation of VFAs from S1, a pasteurized mixture of an organic material, with a very high concentration of VFAs (>17 000 mg/L), showed a total loss of 95% of VFA in the oven-dried sample (dissolved dried sample) compared to non-dried sample (wet sample). The highest concentration of acids in substrate S1 was observed for acetic acid, which corresponded to approximately 47% of the total concentration of VFAs in the material. The lowest concentration was found for iso-hexanoic acid, which contributed to less than 1% of the total concentrations of the VFAs. Both these VFAs, present at high and low concentrations, as well as other VFAs present in the sample were lost to an almost equal extent during the drying. Consequently, this result indicated that the evaporation of the VFAs was not dependent on the initial concentration of the individual acids in the substrate S1.

Table 6. The concentration of VFAs in substrate S1, before and after the DM-analysis and the VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	8 300 ± 560	460 ± 53	94
Propionic acid	3 100 ± 110	94 ± 21	97
Butyric acid	1 900 ± 230	68 ± 17	96
Iso-butyric acid	300 ± 20	6 ± 5	98
Pentanoic acid	1 300 ± 250	46 ± 13	96
Iso-pentanoic acid	500 ± 20	10 ± 5	98
Hexanoic acid	1 700 ± 400	77 ± 21	96
Iso-hexanoic acid	100 ± 6	5 ± 3	96
Heptanoic acid	200 ± 10	10 ± 6	92
Sum VFA (mg/L)	17 000 ± 570	780 ± 140	95

The pH of material S1 was measured prior to the drying and was found to be 5.2. After the drying the pH was found to be 5.9. This increase in pH indicates that the composition of substrate S1 had changed during the drying. The increase in pH could be partly explained by the loss of VFAs but there are many other compounds, in addition to VFA, that can have an influence on the pH, such as the ammonium/ammonia system as well as the carbonate system. Consequently, it is likely that the change in pH is not only due to the evaporation of the VFAs.

3.4.2 *Substrate S2*

Substrate S2 initially contained 4 300 mg VFA/L, of which acetic acid was the dominating acid (Table 7). Despite the fact that the substrates S2 and S1 have a similar origin, the VFA concentration was about 4 times higher in S1 compared to S2. The observed volatility of VFA was 99% during the DM analysis of substrate S2 (Table 7). This is a slightly higher volatility compared to sample S1. Moreover, an increase in pH was detected during the DM-analysis for S2 from a pH of 5.0 to 5.8, in agreement with the observed change in pH for substrate S1.

Table 7. The concentrations of VFAs in substrate S2, before and after the DM-analysis and the VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	2 600 ± 0	49 ± 11	98
Propionic acid	660 ± 10	0 ± 0	100
Butyric acid	470 ± 21	3 ± 1	99
Iso-butyric acid	70 ± 3	0 ± 0	100
Pentanoic acid	220 ± 9	0 ± 0	100
Iso-pentanoic acid	100 ± 20	0 ± 0	100
Hexanoic acid	110 ± 16	0 ± 0	100
Iso-hexanoic acid	20 ± 1	0 ± 0	100
Heptanoic acid	30 ± 3	0 ± 0	100
Sum VFA (mg/L)	4300 ± 61	52 ± 11	99

3.4.3 *Substrate S3*

The silage (substrate S3) had a different origin compared to the substrates S1 and S2, which were pasteurized food and slaughterhouse mixtures. The VFA profile of S3 was shown to be very different from S1 and S2. The substrate S3 contained only acetic acid (99%;

Table 8), while the substrates S1 and S2 contained all of the VFAs. The total VFA concentration, within the substrate S3, was 6 500 mg VFA/L. During the DM-analysis of the substrate S3, 97% of the VFAs were evaporated (

Table 8). This is in line with the results from samples S1 and S2 but higher than the results presented by Porter and Murray (2001), which observed a volatility of approximately 89%. However, in this study, the silage was heated at 100°C for 16 hours, thus another oven-drying method was used compared to the one in this study. Analogic to the observed results in the substrates S1 and S2, the pH increased during the DM-analysis from 4.1 to 4.8.

Table 8. The concentration of VFA in substrate S3 before and after the DM-analysis and the VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	6400 ± 0	190 ± 56	97
Propionic acid	2.0 ± 5	1.0 ± 2	–
Butyric acid	16 ± 1	0 ± 0	100
Iso-butyric acid	0 ± 0	0 ± 0	–
Pentanoic acid	0 ± 0	0 ± 0	–
Iso-pentanoic acid	0 ± 0	0 ± 0	–
Hexanoic acid	23 ± 0	0 ± 0	100
Iso-hexanoic acid	0 ± 0	0 ± 0	–
Heptanoic acid	0 ± 0	0 ± 0	–
Sum VFA (mg/L)	6 400 ± 4	190 ± 57	97

* The uncertainty in the concentration of propionic acid in the silage was very high since the results varied very much between the three independent samples. Consequently, it would be incorrect to calculate the volatility based upon these results.

Silage normally contain higher concentrations of lactic acid compared to VFAs, alcohols and ammonia-nitrogen. The volatility of lactic acid in silage has however been found to be lower (<38%) than VFAs, ammonia and alcohols (Porter & Murray, 2001; Weißbach & Strubelt, 2008a). In this study, the volatility of lactic acid for S3 was however not analyzed.

3.4.4 *Substrate S4*

The initial VFA concentration in S4 (3 000 mg VFA/L), was lower than the other analyzed substrates. It was found that almost all of the VFAs were lost during the DM-analysis, giving a volatility of 100%, when considering the total concentration of VFA (Table 9). This is in agreement with the observed results for S1, S2 and S3. The pH was increased in S4 during the DM-analysis, from pH 4.6 to 5.3, in agreement with results obtained for the other analyzed substrates.

Table 9. The concentration of VFA in substrate S4 before and after the DM-analysis and the calculated volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	940 ± 39	0 ± 0	100
Propionic acid	890 ± 0	4 ± 1	100
Butyric acid	640 ± 26	0 ± 0	100
Iso-butyric acid	10 ± 1	0 ± 0	100
Pentanoic acid	390 ± 24	3 ± 1	99
Iso-pentanoic acid	30 ± 2	0 ± 0	100
Hexanoic acid	63 ± 3	1 ± 0	98
Iso-hexanoic acid	0 ± 0	0 ± 0	–
Heptanoic acid	5 ± 0	0 ± 0	100
Sum VFA (mg/L)	**3 000 ± 19**	**8 ± 2**	**100**

3.4.5 *Digestate D1*

The concentrations of the analyzed VFAs in the wet and dissolved dried samples of digestate D1 are summarized in Table 10. The initial total concentration of VFA was approximately 320 mg/L, with the highest concentration of acetic acid (~88%) among the VFAs. A low VFA concentration in the digestate is typically for biogas digesters with high process efficiency and stability.

A higher total concentration of the VFAs was observed after the DM-analysis compared to the initial concentration (Table 10). It seems unlikely that VFAs have been formed during the drying, but in cannot be ruled out. However, due to the low VFA concentration the uncertainty in the VFA analysis is quite high. Consequently, there might not be a difference in the VFA concentrations between the wet and dissolved dried samples but merely an effect of the uncertainty in the methodology. This result is expected since the pH in the sample was 7.9 and was increased to 9.4 during the drying. Both pH are however higher than the pKa for the VFAs.

Table 10. The concentration of VFA in digestate D1 before and after DM-analysis and VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	280 ± 14	300 ± 18	0
Propionic acid	13 ± 2	25 ± 2	0
Butyric acid	7 ± 0	11 ± 1	0
Iso-butyric acid	4 ± 0	5 ± 0	0
Pentanoic acid	0 ± 0	4 ± 1	0
Iso-pentanoic acid	8 ± 1	7 ± 1	13
Hexanoic acid	3 ± 3	7 ± 1	0
Iso-hexanoic acid	0 ± 0	2 ± 0	0
Heptanoic acid	0 ± 0	7 ± 1	0
Sum VFA (mg/L)	**320 ± 13**	**370 ± 18**	**0**

3.4.6 *Digestate D2*

The initial sample of the digestate D2 contained mainly acetic acid, which corresponded to approximately 88% of the total VFA concentration (Table 11). The concentrations of the rest of the VFAs, i.e. propionic acid, butyric acid, iso-butyric acid, pentanoic acid, iso-pentanoic acid, hexanoic acid, iso-hexanoic acid and heptanoic acid, were very low. Consequently, the uncertainties of the concentrations of these acids were high, as for sample D1. However, as the concentrations of those acids were low, they will thus not have a large impact on the final result. The pH of the initial sample of D2 was found to be 7.9. Despite the fact that D1 and D2 had similar VFA profile and the same initial pH, a difference in the volatility was observed. The volatility of the VFAs in D2, considering the total concentrations of VFAs, was calculated to be 18%. This volatility was higher compared to the VFA volatility for D1 (0%). A volatility of 18% is however negligible, when considering errors in the DM and VS values, as the initial concentration of VFA was low. During the drying, the pH was increased to 8.2.

Table 11. The concentrations of VFAs in the digestate (D2) before and after the DM-analysis and the VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	400 ± 28	310 ± 29	23
Propionic acid	26 ± 4	24 ± 4	8
Butyric acid	9 ± 2	9 ± 1	0
Iso-butyric acid	7 ± 1	5 ± 1	29
Pentanoic acid	0 ± 0	3 ± 0	0
Iso-pentanoic acid	8 ± 1	4 ± 3	50
Hexanoic acid	3 ± 3	6 ± 1	0
Iso-hexanoic acid	0 ± 0	1 ± 1	0
Heptanoic acid	0 ± 0	4 ± 4	0
Sum VFA (mg/L)	450 ± 33	370 ± 37	18

3.4.7 *Digestate D3*

Digestate D3 was withdrawn from a biogas reactor suffering from accumulation of VFA, indicating that the biogas process was suffering from in imbalance (Ahring et al., 1995). The total concentration of VFAs was much higher in the D3 sample (7 700 mg/L; Table 12) compared to D1 (320 mg/L) and D2 (460 mg/L). Moreover, even in spite of high concentration of VFA, the pH was, due to high buffering capacity (data not shown), high (pH 8). During the drying, the pH was decreased down to 6.3.

   The overall VFA volatility for D3 was calculated to be approximately 55% (Table 12), which is higher compared to the VFA volatility for D1 (0%) and D2 (20%). Consequently, the highest VFA volatility was observed for the digestate with the highest initial concentration of VFAs. Even though the initial pH (8.0) in D3 was high, 55% of the VFAs were still lost during the drying. However, the pH within the dried sample was 6.3, which theoretical would give increased evaporation, and thereby supports the results achieved in D3 compared to D1 and D2. Why the pH was decreased in not obvious, however, a theory is that ammonium is evaporated

before the VFAs. If that is the case, loss of ammonium (through ammonia) will result in decreasing pH in the sample during the drying, and thereby increasing the VFA volatility.

All in all, the results from the three digestates shown that the volatility is both depending of the initial pH, the pH after drying and the buffer capacity of the sample. A generalization of the volatility of different digestates is therefore difficult to achieve without doing the same measurements for each individual digestates as in the present study.

Table 12. The concentrations of VFAs in digestate D3 before and after DM-analysis and VFA volatility. The mean values are presented with a 95% confidence interval and the volatility has been calculated according to Equation 7.

Volatile fatty acid	Wet sample (mg/L)	Dissolved dried sample (mg/L)	Volatility (%)
Acetic acid	6 500 ± 170	2 900 ± 120	55
Propionic acid	370 ± 3	210 ± 4	43
Butyric acid	60 ± 2	77 ± 1	0
Iso-butyric acid	300 ± 120	90 ± 3	70
Pentanoic acid	6 ± 1	31 ± 1	0
Iso-pentanoic acid	400 ± 21	100 ± 6	75
Hexanoic acid	5 ± 2	40 ± 2	0
Iso-hexanoic acid	18 ± 0	8 ± 0	56
Heptanoic acid	0 ± 0	6 ± 0*	0
Sum VFA (mg/L)	7 700 ± 200	3 500 ± 120	55

3.5 Errors in process parameters due to VFA evaporation

The evaporation of VFAs during the DM-analysis of the different analyzed samples was shown to be significant. The volatility of the VFA in substrates was between 95-100% (Table 13), which clearly highlights the problem with the evaporation. The results from the analysis of the evaporation of VFAs of the digestate samples were more difficult to interpret as the results varied from 0-55% evaporation.

Since calculations of central process parameters are based upon the DM and VS content it is essential that they are correct. By knowing the volatility of the VFA, compensation can be made and more correct DM and VS values can be calculated. Calculated compensated DM (from hereby called DM_{comp}) and VS (from hereby called VS_{comp}) values are presented in Table 13. This table also includes calculations of the errors in DM (DM_{error}) and VS (VS_{error}) i.e. errors depending on the DM, VS, VFA concentration and the volatility of the VFA. The DM_{error}, which is the relative difference between DM and DM_{comp}, varied between approximately 3-23% and the VS_{error} varied between 3-31% for the analyzed substrates. The evaporation of other volatile organic molecules than VFA is not included since only VFA was measured. The error in DM and VS may therefore be even higher.

The DM_{error} and VS_{error} were shown to be of minor importance for the digestates D1 and D2, which contained low concentrations of VFAs. However, the DM_{error} and VS_{error} were for the digestate S3 was approximately 10% and 14%, respectively.

Table 13. Calculated DM$_{comp}$ and VS$_{comp}$ values after compensation for the VFA evaporation. The errors in the DM and VS values are also shown.

Sample	VFA (g/L)	DM (%)	VS (% of DM)	VFA$_{vol}$ (%)	DM$_{comp}$ (%)	VS$_{comp}$ (% of DM)	DM$_{error}$ (%)	VS$_{error}$ (%)
S1	17	7.2	75	95	8.9	80	23	31
S2	4.3	14	91	99	14	92	3	3
S3	6.5	23	91	97	24	91	3	3
S4	3.0	3.6	99	100	3.9	99	8	8
D1	0.3	3.4	56	0	3.4	56	0	0
D2	0.5	4.7	73	18	4.7	73	0	0
D3	7.7	4	77	54	4.4	79	10	14

Calculations of the OLR using VS (not corrected) of the four different substrates (S1–S4) showed 3–31% higher value compared to calculations using the compensated VS content (Figure 4, Table 12). Substrates S1 and S2 originated from two different plants with pasteurization and the origin of the ingoing materials digested are relatively similar. However, the error in OLR is only 3% for substrate S2, but as high as 31% for substrate S1 (Figure 6; Table 13). This clearly shows that is not possible to generalize the error for a substrate mixture, without actually knowing the VFA concentration. It is therefore important to continuously analyze VFA within the substrate mixture to be able to calculate a correct OLR. A constant OLR over time increases the process stability and that might be hard to achieve without compensating the DM and VS values for the VFA evaporation, particularly if the VFA levels in the substrate are varying a lot.
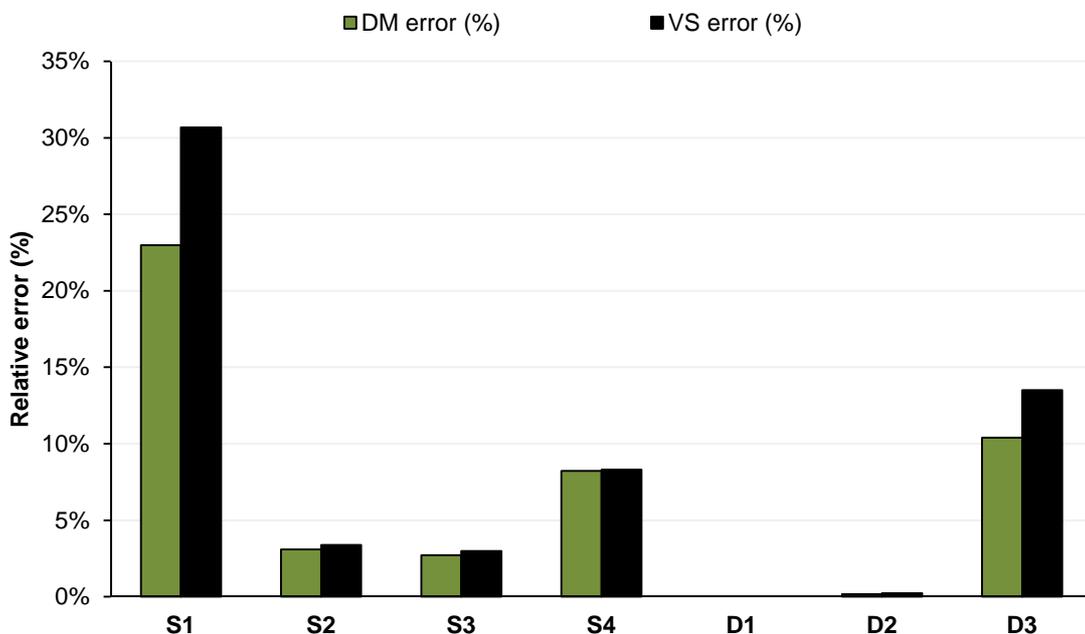

Figure 6. The relative error in the VFA compensated values of DM (DM$_{comp}$) and VS (VS$_{comp}$) compared to the measured DM and VS values.

Calculation of specific biogas production with non-corrected VS values will results in the same relative error as the OLR calculation. This can be exemplified by assuming the "true" specific gas production for S1 and S2 (e.g. 0.70 Nm^3/kg VS). Without compensating for the VFA evaporation, the specific biogas production will

be 0.92 Nm^3/kg VS and 0.72 Nm^3/kg VS for S1 and S2, respectively. This means that one would assume that the substrate S1 had 28% higher biogas potential than substrate S2, which is incorrect. The error (VS$_{error}$) caused by the VFA evaporation within the substrate will result in false-high specific biogas production and could thereby lead to incorrect judgment concerning the economic value of a specific substrates for a biogas plant.

Using different VS values and calculating the degree of degradation, illustrates that the error might even be higher than the errors in the parameters OLR and specific gas production. This is caused by the fact that both the DM and VS of the inlet substrate as well as the DM and VS of the digestate are used in this calculation. In a scenario when a substrate with a high concentration of VFA is digested, thus giving a risk that VFA also is being accumulated in the digester, the calculation may results in a "double" false value. This can be exemplified by assuming a hypothetical biogas plant where substrate S1 is fed into the digester, and D3 is the outlet digestate. With a compensation of the VFA evaporation in the measurement, in the substrate as well as in the digestate, the degree of degradation will be 51%. When doing the same calculation but with a VFA compensation for the VS content of the substrate only and not for the digestate, a false-high value of 56% is obtained. Without any VFA compensation at all, the degree of the degradation will on the contrary have a false-low value of 43%.

All in all, it is of great importance to take the error in the DM and VS into consideration when performing calculation of organic loading rate, specific biogas production as well as the degree of degradation. However, the error may be negligible for some substrates and biogas plants (e.g. digestion of substrate S2 or S4) but essential for other plants with high VFA content in the substrate (e.g. digestion of S1 or S3).

3.6 Evaporation of ammonium during the dry-matter analysis

The main focus of the present project was to evaluate the evaporation of VFAs, during the DM-analysis using oven-drying. However, both the substrates and digestates also contain inorganic molecules, such as ammonium and ammonia, which can affect the DM results. The total concentration of ammonium (NH$_4$-N) was analyzed in the samples before and after the DM-analysis and the observed results are presented in Table 14 and in Figure 7. It should be notified that the presented values include both the concentration of ammonium in the NH$_4$-N state as well as the NH$_3$-N state but will hereafter just be called NH$_4$-N.

A common value of ammonium concentration in the digestate from a co-digestion plant is approximately 3 g NH$_4$-N/kg, exemplified by the samples D1 and D2 (Table 14). Ammonium and ammonia is in equilibrium with each other, with an increasing fraction being ammonia with increasing pH and temperature. In a mesophilic process (~37 $^\circ$C), about 10% of the total ammonium fraction is in the ammonia state. However, in the oven-drying, the temperature rises to 105°C and will more or less dislocate the equilibrium to ammonia (boiling point -33°C), which is highly volatile. By using the formula given by (Hansen et al., 1998) and a typical pH of a digestate, 7.5, the oven-drying at 105°C will result in 61% of the total NH$_4$-N being in the NH$_3$-N state. Thus, more or less all ammonium and ammonia can be expected to be evaporated in the case of a digestate. However, in a substrate less than 1% of the ammonium is expected to be in NH$_3$-N state, due to a lower pH (typically 4-5).

Table 14. The concentration of ammonium (NH$_4$-N) in wet and dissolved dried samples of the substrates S1-S4 and digestates D1 and D2. The mean values are presented with a 95% confidence interval and the volatility has been calculated by the same principle as the volatility of the VFAs (Equation 7).

Sample	Wet sample (mg NH$_4$-N/L)	Dissolved dried sample (mg NH$_4$-N/L)	Volatility (%)
S1	1 400 ± 39	27 ± 3	98
S2	510 ± 140	10 ± 6	98
S3	450 ± 210	390 ± 48	13
S4	48 ± 5	3 ± 1	94
D1	2 900 ± 120	4 ± 1	100
D2	2 800 ± 65	49 ± 9	98

The analysis showed the highest concentrations of NH$_4$-N for D1 (~2.9 g NH$_4$-N/kg) and D2 (~2.8 g NH$_4$-N/kg). Both digestate D1 and D2 had a pH of 7.9 in the wet samples. The tested substrates contained between 0.05 to 1.4 g NH$_4$-N/kg and the pH varied from 4.1 to 5.2. It was thus observed that the pH was highly correlated with the NH$_4$-N concentration with a linear correlation of 96%. This showed that samples with high levels of ammonium had a higher pH than substrates with low NH$_4$-N concentrations. In spite of the variation in pH, the volatility of ammonium was shown to be ≥94% in S1, S2, S4, D1 and D2. The results also indicated that the ammonium volatility was lower in S3 (~13%) compared to the other materials. In a previous published study by Porter and Murray (2001), the volatility of ammonia was found to be >97% in grass silage that was heated. It seems unlikely that there would be such a large difference in the volatility of ammonium in the grass silage included in this study compared to the study published by Porter and Murray (2001).The silage was more complicated to analyze since the DM was much higher than the other analyzed materials and the S3 had to be mixed with water prior to the analysis of the wet (initial) ammonium concentration. It is possible that not all of the ammonium was detected in the wet sample. The uncertainty was also very high in the measurements of the wet sample of S3 (Table 14), which is an indication of an inhomogeneity with respect to the ammonium concentration.
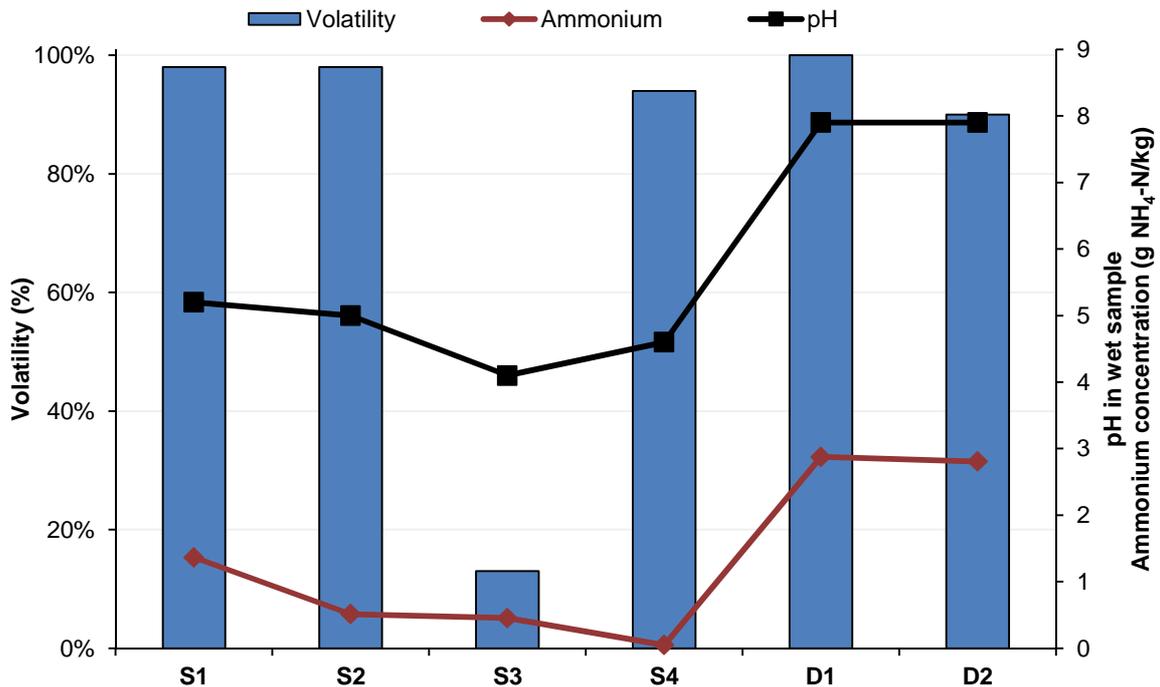
Figure 7. Volatility of ammonium within the different samples complied with the pH and ammonium concentration of the wet samples (before drying).

3.7 The volatility of VFA – a summary of the observed results

As discussed previously, the VFA volatility was higher than 95% in all four substrates (Figure 8). The volatility was lower for all the three digestates compared to the four substrates and there were a significant difference between the digestates, being approximately 0, 18 and 55% for D1, D2 and D3, respectively. For the digestate samples the highest volatility of the VFAs was found for the digestate with the highest total VFA concentration. However, it should be noticed that for materials with very low concentrations of VFAs such as the digestate D1 and D2 the uncertainty in the analyzed VFA concentrations was large.
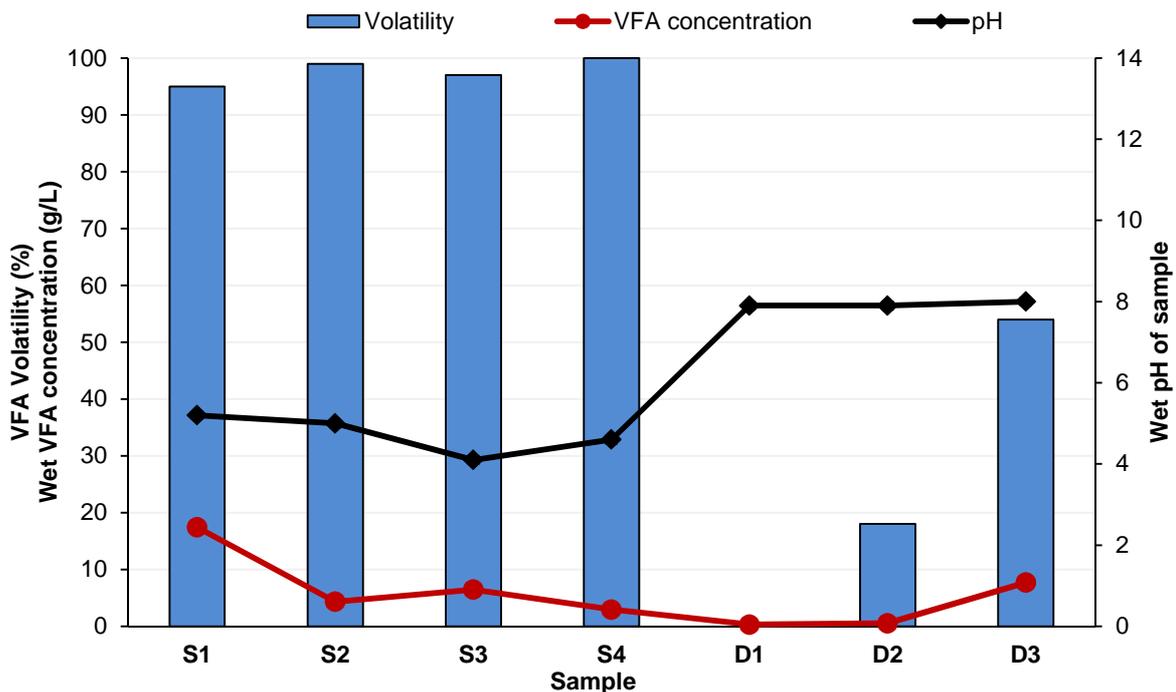
Figure 8. The volatility of VFA, the pH and the total concentration of VFAs in the four analyzed substrates and the three investigated digestates.

When comparing the volatility of VFAs of substrates and digestates it is clear that pH is an important parameter. The volatility was much higher for the substrates with low pH than the digestate that had a much higher pH. The importance of pH for the degree of evaporation was also shown in the experiments performed to verify that it was possible to detect a majority of the VFAs in dissolved dried samples diluted in MilliQ water (Chapter 3.2). The volatility was 95% in sample S1 with a pH of 5.2 and 2% when the pH had been increased to above 11. The same trend was observed for S2 sample for which the volatility was 99% (pH 5.0) compared to 19% when the pH was above 11. Consequently, these results showed that the evaporation of VFAs can be minimized by modifying the pH. Negatively charged VFAs might interact with positively charged molecules or substances within the material and the evaporation of the VFAs is consequently minimized.

The substrates used for biogas production are highly complex and diverse at a molecular level. Consequently, even when comparing similar types of substrates originating from different full scale plants, these materials will be different at the molecular level. It is thus likely that different reactions and composition changes will occur within different materials during the drying process and this might in turn have an impact of the evaporation of the volatile compounds. This was for example observed in this project as the pH of the analyzed materials changed differently in different samples during the oven DM-analysis. Consequently, the evaporation of volatile molecules from a sample might influence the volatility of the molecules still in the sample. It is difficult to clearly reveal what chemical property of the materials or what environmental factor that will have the most effect on the evaporation of VFA and ammonia.

3.8 Methods to compensate DM for VFA evaporation biogas substrates

For someone in the business of biogas production that would like to adopt the findings in this study, two methods for compensation are suggested when analyzing DM with oven-drying.

As stated earlier, the impact of the discrepancy in the analysis is dependent on the characteristics of the materials analyzed. For materials, typically substrates streams, with a low pH (<5.2), there is probably a high risk that the majority of the VFA is lost during the oven DM-analysis. This might be a large problem when the analyzed material has a high concentration of VFAs in relation to the DM, as the error in VS-weight in this case would be very large. Therefore, there are no quick fix of this problem and no general rules to adopt for all types of materials.

An original thought was to prove a method decreasing evaporation of VFA by adding NaOH and thus increase the pH. The VFAs would then be fixed in the sample and by considering the amount of added NaOH, contributing to DM and it would then be possible to obtain a correct DM and VS value. This method would be relatively easy to adopt for operators at a biogas plant or in a laboratory. However, even if the VFAs could be fixed into the samples during the DM-analysis, the addition of NaOH caused false-high DM values, probably due to other chemical reactions within the sample. Modification of pH by adding NaOH to minimize the evaporation of VFAs has also been investigated by (Nordberg et al., 2010) which observed a lower experimental DM value than expected for artificial substrates.

Therefore, the suggested methods for correction DM are more complicated and include more analysis of the material of interest than expected and hoped for before performing this study. As other volatile molecules, besides VFA, might be present in the materials, these should also be compensated for to obtain exact DM and VS values. More accurate DM and VS values are however obtained by using the suggested method to compensate for the VFA loss than without compensation. For substrates with low pH, both methods can be applied. Since the variation in results for evaporation of VFA in the digestate, only method 2 should be applied. The suggested methods give different accuracy of the DM_{comp}.

3.8.1 *Method 1 - Rough estimation method*

Method 1 for estimation of DM_{comp} and VS_{comp} is suggested for substrates with low pH (pH ≤ 5.2) and when a rough estimate is sufficient. Analyzes of pH and VFA (as a sum of organic acids or as VFA) are performed on the material (substrate, digestate or mixtures of materials).

1)
Measure DM (DM_m) and VS (VS_m) according to the Swedish Standard method SS 02 81 13 (SIS, 1981): DM determination in oven for 20 hours at 105°C and VS determination of the dried sample for 2 hours at 550°C.

2)
Analyze the concentrations of VFAs in the original sample (VFA_m). This could be done by analyzing the individual VFA and sum them up or by using a quick method that gives the sum directly. The unit of the result used should be: "mg VFA/L".

3)
Assume a value for the volatility of VFAs in your substrate, preferably $VFA_{vol.}$ = 98% (see results and discussion for volatility in different types of substrates). Calculate the compensated DM_{comp} weight by:

$$DM_{comp}\,(\%) = DM_m\,(\%) + \left(\frac{\left(VFA_{volatility}\,(\%) \right)}{100} * VFA_m\,(mg/L) * 10^{-4} \right)$$

4)
Calculate VS_{comp} (% of DM_{comp}) by:

$$VS_{comp}\left(\%\ of\ DM_{comp} \right) =$$

$$\frac{\left(DM_m(\%) * VS_m(\%)\right) + \left(10^{-4} * VFA_{volatility}\,(\%) * VFA_m\,(mg/L) \right)}{DM_{comp}(\%)}$$

3.8.2 *Method 2 - Detailed estimation method*

This method should be used to compensate for the evaporation of VFAs in those cases where it is important to have a very good estimation of the DM content in a specific substrate or substrate mixture. For digestates, this method only can be used.

1)
Analyze the concentrations of VFAs in the original sample (VFA_m). This could be done by analyzing the individual VFA and sum them up or by using a quick method that gives the sum directly. The unit of the result used should be: "mg VFA/L".

2)
Measure DM (DM_m) and VS (VS_m) according to the Swedish Standard method SS 02 81 13 (SIS, 1981): DM determination in oven for 20 hours at 105°C and VS determination of the dried sample for 2 hours at 550°C.

3)
Add MilliQ water to the beaker containing the dried material. The added amount of MilliQ water (m_{water}) should be adjusted so that the weight of the material is approximately the same as before the drying. Consequently, if 8 grams of materials were inserted in the oven, then the weight of the dried materials dissolved in MilliQ water (m_{water}) should be about 8 grams. The water should however cover the dried material so if e.g. a lot of material is fixed on the wall of the beaker it might be necessarily to add more water.

a) Notice the weight of the dried sample ($m_{sample,dried}$).
b) Let the beaker with the dried material and the added MilliQ water stand for 30 minutes. Then, stir the solution for 10 minutes.
c) Analyze the concentration of VFAs in the dissolved dried material ($VFA_{dried,dissolved}$).
d) Calculate the concentrations of VFAs in the dried material before dissolved in MilliQ water (VFA_{dried})

$$VFA_{dried}\,(mg/L) = VFA_{dissolved,dried} * \left(\frac{(m_{sample,dried} + m_{water})}{m_{sample,initial}} \right)$$

4)
Calculate the actually volatility (%) of the VFAs in the sample:

$$VFA_{volatility}(\%) = \left(1 - \frac{VFA_{dried}\left(\frac{mg}{L}\right)}{VFA_m\left(\frac{mg}{L}\right)} \right) * 100$$

5)
Calculate the compensated DM_{comp} weight by:

$$DM_{comp}\,(\%) = DM_m\,(\%) + \left(\frac{VFA_{volatility}\,(\%)}{100} * VFA_m\,(mg/L) * 10^{-4} \right)$$

6)
Calculate VS$_{comp}$ (% of DM$_{comp}$) by:

$$VS_{comp} \left(\% \: of \: DM_{comp} \right) =$$

$$\frac{\left(DM_m(\%) * VS_m(\%) \right) + \left(10^{-4} * VFA_{volatility} \: (\%) * VFA_m \: (mg/L) \right)}{DM_{comp}(\%)}$$

4   Conclusions

In this study, the evaporation of VFAs and ammonia from different substrates and digestates during DM-analysis using oven-drying were investigated. The results showed that the evaporation of VFAs during the DM-analysis using oven-drying could be a major problem for substrates with a relatively high concentration of VFA in relation to the DM content. Four distinct biogas substrates (3-17 g VFA/L), all with low pH, were evaluated with the respect to VFA evaporation. The loss of VFA during the DM-analysis in oven (20 hours, 105°C) was concluded to be 95-100% for the four substrates. The errors caused by evaporation of VFAs during the DM-analysis may result in a false-high specific biogas production and a false-low organic loading rate. In the present study the measurement errors were in the range of 3-31% for the analyzed substrates. Three different types of digestates were also evaluated (0.3-7.7 g VFA/L), all with high pH, with the respect to VFA evaporation. The evaporation of VFA varied between 0-50% in the digestates. The difference between the substrates and digestates indicated that the pH and buffer capacity of the samples were important factors.

Moreover, a comparison between the concentrations of VFA and the amount of dissolved organic carbon (TOC) for a reference substrate indicated that the majority of the volatile organic material that was lost during the DM-analysis was VFA. Based on the obtained results, two different methods (with different accuracy) to compensate the DM and VS in biogas substrates with low pH and digestates were suggested. Furthermore, it was also shown that also ammonium evaporated from substrates and digestates during the oven-drying. This might be of importance for digested materials where the concentration of ammonium often is high. The evaporation of ammonium should be investigated further to be able to compensate for the loss of this volatile molecule.

All in all, the results from the present study showed that it is of greatest importance to compensate DM and VS for the VFA evaporation that occurs during DM-analysis by oven-drying. By applying one of the methods suggested in this report, more reliable values of specific biogas production and potential organic loading rates could be expected in both full scale and laboratory scale conditions.

5   Acknowledgements

6 Literature

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