Cornell University

PRO-DAIRY

Analytical Procedures for Monitoring Farm-based Anaerobic Digestion (AD) Systems: PROTOCOL I

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Preface

We have developed four protocols of analytical procedures for the monitoring of farm-based anaerobic digestion (AD) systems. The use of either protocol will depend on the scopes and lab resources of the facility, and the time availability of the system operator.

Protocol I is the most basic and simple version of the analytical procedures, designed to evaluate the *performance of manure-only AD systems*. This protocol includes the analyses of total solids (TS) and total volatile solids (VS) in the influent and the effluent of the digester, for the evaluation of waste treatment efficiency of the system.

Protocol II is the upper level of protocol I, intended to monitor the stability of on-farm AD systems with a higher level of complexity; for example, systems co-digesting a single, low-strength co-substrate in its operation, such as whey products, in a systematic or intermittent basis. This protocol includes the analyses of total volatile fatty acids (TVFA) and total alkalinity (TA) for the determination of the TVFA:TA (or FOS:TAC) ratio, and includes the measurements of methane content, pH and temperature. Protocol II requires a more complex laboratory setup and analysis time than Protocol I.

Protocol III is a more comprehensive version of protocol II, developed to monitor the stability of on-farm AD systems that co-digest one or more off-farm, high-strength substrates in a continuous basis, particularly for operations receiving protein-rich substrates. Protocol III includes all the analyses of Protocol II in addition to total ammonia-nitrogen (TAN). Protocol III requires virtually the same laboratory setup and analysis time as Protocol II.

Protocol IV is the most advanced version of the protocol, developed for the monitoring of both performance and stability of on-farm anaerobic digesters with the same characteristics as those described in Protocol III. Protocol IV combines all the analyses included in Protocol I and III, and thereby requires a full laboratory setup and a longer analysis time.

This following document describes the materials and analytical procedures of Protocol I.

Table of Contents

1. Solids analysis: Total Solids (TS), Total Volatile Solids (VS), Total Fixed Solids (FS)

1.1. Apparatus

- *Ceramic crucibles, 100-mL capacity*
- *Drying oven, for operation at 103 to 105°C*
- *Muffle furnace for operation at 550°C*
- *Desiccator and material to absorb moisture from samples*
- *Analytical balance, capable of weighing to 0.01 g*
- *High temperature marker*
- *Tongs*
- *1000-mL plastic bottles with screw caps, for sampling*

1.2. Reagents

No reagents required

1.3. Procedure

1.3.1. Preparation of ceramic crucibles

Turn the muffle furnace on and set the temperature to 550°C. Once the temperature has been reached, ignite all clean ceramic crucibles for 1 h. Next, using the tongs, carefully retrieve the dishes from the furnace and store them in the desiccator until needed.

1.3.2. Sample analysis

a) Turn the drying oven on and set it to 105°C

b) Using 1000-mL plastic containers, collect 1 sample from the digester influent and another sample from the digester effluent (fill the containers up to 1 inch below the top).

c) Create the table below:

Date	***Sample***	***Crucible weight***	***Wet weight***	***Dry weight***	***Ashes weight***
Date 1	Inf A				
Date 1	Inf B				
Date 1	Eff A				
Date 1	Eff B				

d) On the first column, i.e. ***Date****, write down the date of analysis*

e) We will measure duplicate (two) samples for both the influent and the effluent of the digester, so retrieve 4 ceramic crucibles from the desiccator, and label one pair as Inf A and Inf B, and another as Eff A and Eff B

f) Under the second column of your log sheet, i.e. ***Sample****, write down the name of the 4 samples: Inf A, Inf B, etc.*

g) Using the analytical balance, weigh the crucibles one-by-one and write down each weight next to appropriate sample name, and under the column ***Crucible weight***

h) Align the 2 influent sample crucibles (Inf) in a line, and while swirling the influent sample container, fill each crucible up to ½ inch of the top with sample (approximately 75 mL) directly from the container, or using the plastic spoon

i) Weigh crucibles on the analytical balance and record this weight on the log sheet, under the column ***Wet weight***

j) Repeat steps d and e for the next 2 crucibles using the effluent sample

k) Place all the crucibles in the drying oven and evaporate to dryness for at least 8 h, preferably overnight, at 105°C.

l) Using the tongs, collect the crucibles from the oven and put them in the desiccator to balance temperature for 30 min, or until cold to touch; turn the drying oven off if no longer needed

m) In the meantime, turn the muffle furnace on, and set it to 550°C

*n) Take one crucible at a time from the desiccator, weigh on the analytical balance, and record this weight on the log sheet under the column **Dry weight** (note: do not take all the crucibles out of the desiccator at once before weighing)*

o) When the muffle furnace has reached 550°C, place the crucibles inside and ignite them for at least 30 min, preferably 1 h

p) Using the tongs, collect the crucibles from the furnace and put them in the desiccator to balance temperature for 1 h or until cold to touch; turn the muffle furnace off if no longer needed

*q) Take one crucible at a time from the desiccator, weigh on the analytical balance, and record weight on the log sheet under the column **Ashes weight***

r) Enter these data to the spreadsheet to obtain results; keep a hard copy of these results in your lab notebook

1.4. Calculations

1.4.1. Total Solids (TS)

$$TS\left(\frac{g}{L}\right) = \frac{Dry\ Weight\ (g) - \ Dish\ Weight\ (g)}{Wet\ Weight\ (g) - \ Dish\ Weight\ (g)} \cdot 1{,}000$$

$$TS\ (\%) = \frac{TS\ \left(\frac{g}{L}\right)}{10}$$

1.4.2. Total Volatile Solids (VS)

$$VS\ \left(\frac{g}{L}\right) = \frac{Dry\ Weight\ (g) - \ Ashes\ Weight\ (g)}{Wet\ Weight\ (g) - \ Dish\ Weight\ (g)} \cdot 1{,}000$$

$$VS\ (\%) = \frac{VS\ \left(\frac{g}{L}\right)}{10}$$

1.4.3. Total Fixed Solids (FS)

$$FS\ \left(\frac{g}{L}\right) = \frac{Ashes\ Weight\ (g) - \ Dish\ Weight\ (g)}{Wet\ Weight\ (g) - \ Dish\ Weight\ (g)} \cdot 1{,}000$$

$$FS\ (\%) = \frac{FS\ \left(\frac{g}{L}\right)}{10}$$

The average of the three samples should agree within 5% of their average weight

2. Safety

Hard copies of the Material safety data sheets (MSDS) are inside a binder in all labs. MSDSs explain safety protocols in detail, please, make sure to have the bider in a visible and fixed location of the lab

3. Equipment and materials glossary

3.1. Drying oven, muffle furnace

3.2. Analytical balance, desiccator

3.3. Ceramic crucibles

4. List of supplies

The following is a list of the lab supplies that will need to be purchased by the farms when the initial supplies are exhausted. The table includes the suppliers' information and the product number.

	Brand/model	Provider	Characteristics	Product number
Ammonia pH and ion strength adjuster	Ricca chemical	Fisher Scientific	10 M NaOH, 500 mL	ACCU0802-500A
Ammonia standard	Thermo Scientific	Fisher Scientific	Ammonium chloride for NH3 standard 500 g	FLA661-500
Sulfuric acid	Sulfuric Acid, BAKER ANALYZED Reagent. ACS Grade	VWR	Case of 6 x 2.5-L (95-98% purity)	JT9681-3
Sodium hydroxide	Sodium Hydroxide, Volumetric Solution, BAKER ANALYZED* Reagent. 10N	VWR	Case of 6 x 1-L 10 N (9.95-10.05 N)	JT5674-2
Acetic acid	Acetic Acid, BAKER ANALYZED* Reagent. ACS Grade	VWR	500 mL bottle (99.7% purity)	JT9508-2
Desiccants	Drierite, with indicator, 4 mesh, Acros Organic	Fisher Scientific	500 g, 4 mesh (4.75 mm), with indicator	AC21908-5000
Crucibles	VWR Low Form Porcelain Crucibles	VWR	100 mL (dimensions: 76D x 46H mm)	89038-030
High temperature marker	MARKING PEN DEPOTDYKEM 44 HI TEMP MARKER BLACK	Fisher Scientific	Black	44250