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Application of Thermogravimetric Analysis for the Proximate Analysis of Livestock Wastes

ABSTRACT: There is worldwide interest in deriving increasing amounts of energy from bio-based agricultural materials including not only lignocellulosic residues but also a significant quantity of available livestock manure. This manure can be used as a feedstock for various thermochemical conversion processes such as pyrolysis and gasification. In order to apply these processes, the manure must be properly characterized for volatile matter (VM) and ash contents. The determination of these components is not mentioned specifically in current ASTM standards for livestock manure. In this study, we employed the use of thermogravimetric analysis (TGA) for the rapid assessment of VM and ash content in swine, dairy, rabbit, and poultry manures using references from the ASTM coal and coke standards. The TGA assessment of VM in the manures were the same as those values found by non-automated means (ASTM D3175-07) ranging from 47 to 78 wt%$_{db}$. The TGA assessment of the ash was also the same when compared to ash results via non-instrumental means following ASTM D3174-04. Ash values ranged from 4 to 47 wt%$_{db}$. There was one exception when testing a high ash containing swine lagoon sludge. Under the TGA method, this sludge underwent more complete devolatilization and oxidation. This was primarily attributed to the small sample size leading to uniform internal heating. The modification of the TGA ash method aimed at shortening the run time generated similar results as both the original TGA method and non-automated method. Thus, TGA ash determination in manure should occur above 600°C with preferences for the following method: Zero-grade air at 2–4 furnace volumes/min, heating rate of 11°C·min−1, temperature range of 110–950°C, and isothermal hold at 950°C for 10 min. VM determination via TGA should follow ASTM D3175-07.

KEYWORDS: instrumental analysis, animal manure, volatile matter, ash, standard method

Introduction

Alongside the massive consolidation of concentrated animal feeding operations (CAFOs) over the past few decades, there has been a significant increase in the concentration of animals that generates large quantities of not only spent bedding materials but also manure and wastewater [1]. Traditional manure management practices have recycled plant nutrients through land application. Unfortunately, manure production from CAFOs is often greater than local crop and proximal pastureland nutrient demands. Overapplication of the animal manure can impose potential environmental threats: Spread of pathogens, release of hormones and odorous compounds, and nitrogen and phosphorous contamination of surface and ground waters leading to eutrophication [2–4]. In addition to these environmental threats, the agriculture industry is faced with rising energy prices and concerns over petroleum supplies [5]. Thus, there is expanded interest in using livestock manure as a bioenergy feedstock. Utilizing animal manures in this manner will lead to on-farm biofuel production and concomitantly evolve into new state-of-the-art waste management systems, thereby creating environmentally benign livestock operations [5]. Annually, animal production generates 31.75 Mtons (35 million dry tons) of sustainable biomass/manure feedstock; this amount comprises 18 % of the total available sustainable biomass from U.S. agricultural lands [6]. While anaerobic digestion is a well established method of waste treatment and energy conversion [7–9], there is considerable interest in alternative waste treatment systems using the thermochemical conversion (TCC) processes of pyrolysis, gasification, and direct liquefaction [5,10–15]. When making a selection from these options, it is important

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TABLE 1—*ASTM standard test method for VM analysis summary for various substrates including PWF, AC, coal, and RDF.*

Method	Feedstock	Mass (g)	Temperature (°C)	Hold Time (min)
D1762-84 [36]	Wood charcoal	1	(1) 300, (2) 500, (3) 950[a]	(1) 2, (2) 3, (3) 6
D3175-07 [31]	Coal and coke	1	950 ± 20	10
D5832-98 [37]	AC	1	950 ± 25	7
E872-82 [20]	PWF	1	950 ± 20	7
E897-88 [38]	RDF	1	950 ± 20	7

[a]Temperature adjustment requires manually placing the covered crucible at different lateral positions in the muffle furnace.

to consider the economics, final end product form (i.e., gas, bio-oil, or char), availability of the feedstock, and the feedstock characteristics [5,16,17].

In order to effectively utilize manure or any biomass in a TCC process, the following feedstock compositions should be known: Moisture content (MC), volatile matter (VM), fixed carbon (FC), and ash. These components can be determined following a proximate analysis method. This method directly determines VM and ash on a dry-basis (db), while FC is determined by their difference. These values can easily be transformed into an as-received basis at the determined MC following ASTM D3180-89 [18]. Proximate analysis ASTM methods and standards have been written for a variety of feedstocks: Wood, activated carbon (AC), and coal (Tables 1 and 2). The ASTM standards also include detailed methods for categories of feedstocks. For example, refuse-derived fuels (RDFs) include discarded waste used as a fuel as well as combustible waste fractions prepared according to size—coarse particle (with and without metal), particle size of less than 5.08 cm (2 in.), and powder form [19]. Particulate wood fuel (PWF) also has examples—sawdust, green tree chips, and pellets [20]. Lastly, biomass, as defined in ASTM E1755-01 [21], is an all encompassing term that includes the following: Feedstocks from herbaceous materials, hard and soft woods, agricultural residues (e.g., corn stover, wheat straw, and bagasse), solid fermentation residues, and wastepaper. Among all these defined feedstocks, there is no mention of livestock manure and their blends.

With future waste-to-energy-generation processes likely processing livestock manure, there is the need to characterize manure generated in its various forms (e.g., livestock house effluent, separated solids, and anaerobic sludge) with respect to its VM and ash contents. Livestock manure's VM and ash contents can be effectively assessed using thermogravimetric analysis (TGA). Simultaneous TGA and differential thermal analysis (DTA) has proven to be a useful tool in other bioenergy feedstocks conversion mechanisms [22–24]. The TGA technique at a laboratory-scale uses a small amount of sample (milligram), continuous supply of carrier gas (reactive gas), and programmable heating rates. The small sample size allows the sample to undergo faster uniform heating than gram-size samples, thereby reducing the length of time required to perform standard analyses as well as leading to a higher throughput. This is in contrast to the general requirements by traditional ASTM standards: Larger sample size and the few hours long run times

TABLE 2—*ASTM standard test method for ash analyses summary for various substrates including PWF, AC, coal, and RDF.*

Method	Feedstock	Mass (g)	Temperature (°C)	Ramp (°C/min)	End Conditions
D1102-84 [39]	Wood[a]	2	580–600	NA	30 min, ±0.2 mg
D1762-84 [36]	Wood charcoal[b]	1	750	NA	6 h, ±0.5 mg/h
D2866-94 [40]	AC	0.1[c]	650 ± 25	NA	3–16 h
D3174-04 [30]	Coal and coke	1	(1) 450–500, (2) 700–750 (coal), 950 (coke)	(1) 7.5, (2) 3.3 (coal), 3.75 (coke)	120 min
E830-04 [19]	RDF	1	575 ± 25 or 725 ± 25	NA	±0.001 g/h
E1534-93 [41]	PWF	2	580–600	Slow heat[d]	30 min, ±0.2 mg
E1755-01	Biomass	0.5–1	(1) 250, (2) 575 ± 25	(1) 10, (2) NA	(1)30 min, (2) >180 min [e] and ±0.3 mg

[a]Standard covers ash determination of wood and wood products.

[b]Ash is determined from devolatilized sample (Table 1).

[c]Sufficiently dried AC to result in estimated 0.1 g ash.

[d]Standard states crucible is placed in a cold muffle furnace; then, it is slowly heated to temperature.

[e]If ash is expected to be greater than 5 %, the sample is exposed to 575°C overnight.

TABLE 3—*Animal manure collection site locations, operation type, sample description, and as collected TS content.*

			Samples	
Site	Location	Operation	Description	As Collected TS (%)
1	Sampson Co., NC	Swine[a]	Homogenized flushed manure house effluent	1.1
			Rotary press separator with flocculant	25
			Anaerobic lagoon sludge	9
2	Prince George's Co., MD	Dairy[b]	Mechanically scrapped dairy manure	12
			Screw-press separator solids	24
3	Highland Co., OH	Rabbit	Caged manure pellets	87
			Composted manure (3–4 years)	30
4	Sumter Co., SC	Poultry[c]	Soiled poultry litter	17

[a]Reference 42.
[b]Reference 43.
[c]Reference 44.

(Tables 1 and 2). While most traditional standard methods are non-automated or manual in nature, there are some ASTM standards that address the use of instrumental TG analysis for VM and compositional analysis—ASTM E1868-04 and E1131-08 [25,26].

The ASTM E1868-04 standard test method [25] describes a procedure using thermogravimetry to determine the amount of VM removed from a solid or liquid sample under a specific and pre-determined set of temperature and time conditions. Essentially, a sample of known mass is heated at a constant temperature ramp over a pre-determined time interval or until the rate of mass loss has achieved a desired value. At the end conditions, the mass loss is reported as the loss-on-drying (LOD). This parameter is identified as a function of both time and temperature. The method gives examples of a reported LOD value as either LOD=*XX* % (2 h at 105°C); this is based on an isothermal test temperature over a fixed period of time, or in the instance where the rate of achieved mass loss is the criteria, the LOD value would be reported as *XX* % (15 min at <1 %).

The compositional analysis by thermogravimetry as described in ASTM E1131-08 [26] is applicable to solid and liquid samples (10–30 mg) and used to determine the amount of high and medium VM, combustible material, and ash content. This method utilizes inert and reactive gases within the same run, specifying when gas switchover occurs as well as necessary isothermal periods. For this method, the mass loss in an atmosphere within a specific temperature range provides the compositional analysis. The determination of the ash content is found after the gas switchover from nitrogen to air when either of the following takes place: (1) A mass loss plateau is established in the range of 600–950°C or (2) the first derivative has a zero slope at a pre-determined temperature. Reported method parameters such as gas flow rate, heating rate, and gas switchover temperatures are qualified to be guidelines and can be altered to suit a particular analysis. This assumes that one reports the modified method. The ASTM E1131-08 method suggests an analysis for coal: Sample size of 20 mg, gas flow rate of 50 mL/min, temperature profile of ambient to 110°C between 10 and 150°C·min^{-1} to 900°C, and gas switchover from nitrogen to air occurring at 900°C.

In this work, we demonstrate the use of TGA techniques following current ASTM standard methods for determination of the VM and ash content of various livestock manures. These values are compared to those ASTM standard methods that are non-instrumentally determined. Also presented are results from a modified TGA method for the accurate analysis of livestock manure samples. Results from this work can contribute toward the creation of new ASTM standard methods for VM and ash content determinations in livestock manures.

Experimental

Materials and Sample Preparation

Animal manure samples were acquired from swine, dairy, rabbit, and poultry operations (Table 3). In addition to collecting unaltered manure samples, other manure samples were collected in order to represent

the varied forms generated after waste treatment (e.g., solid liquid separation and composting). These treatment processes can generate a material with a total solid (TS) content ranging from 9 % to 30 %. All samples were oven dried at 105°C to remove all moisture, then fine ground to pass through a 60 mesh sieve (250 μm). From each material, duplicate or triplicate subsamples were sent to an independent facility (Hazen Research, Inc., Golden, CO) for proximate analysis following ASTM D3172-02 [27]. This method was noted to be modified for biomass in that the ash was produced and assessed at 600°C.

Thermogravimetric Analysis Set-Up

The thermogravimetric system used in this investigation was a TGA/SDTA851e (Mettler Toledo International, Inc., Columbus, OH) equipped with the following: A microbalance, a high temperature furnace capable of reaching 1600°C, an automatic sample robot, a GC200 gas controller, and a circulating water bath regulated at 22°C. The TGA was operated from a PC equipped with STARe software v. 9.10 (Mettler Toledo International, Inc., Columbus, OH). This unit was capable of simultaneously recording mass loss (TGA) and temperature changes (DTA).

The annual maintenance of the instrument included testing and calibration of the internal scale; the monthly maintenance included a three-point temperature calibration using the melting points of indium, aluminum, and gold; and the weekly maintenance included refilling the water bath and cleaning the furnace. The furnace was cleaned using water and cotton swabs, then baked for 20 min at 1200°C; this was performed to remove the regular build-up of condensed VM and tars. If samples were high in VM, the furnace was baked out more frequently. The 70 μL AlO_3 crucibles and their lids were cleaned using swabs, water, and detergent, thoroughly rinsed using deionized water, and baked at 550°C for 1 h in an oven.

To reduce the effects of environmental noise, this entire unit was encased in a rectangular structure to reduce the influence of sudden pressure changes and temperature changes (e.g., opening of exterior doors and drafts from HVAC units). This unit was also on an isolated electrical ground to prevent large current switching—particularly from HVAC units—from influencing electrical signals in the microbalance. The TGA unit was placed on a heavy anti-vibration slab away from countertops in contact with exterior walls. This was implemented to ensure that operation was not affected by vibrations from HVAC units. These units were left on to regulate the room temperature and to prevent overrunning the cold water bath.

Thermogravimetric Analysis Operation

A specific sample preparation routine was used prior to the TGA runs. The 70 μL AlO_3 crucibles were stored in a desiccator to prevent variable moisture accumulation. Once the 70 μL AlO_3 crucibles were loaded with oven-dried samples, the samples were subjected to the following drying program: A hold temperature of 110°C for 15 min under zero-grade air at a flow rate of 80 $mL \cdot min^{-1}$. This flow rate was more than twice the furnace volume per minute as recommended for all determinations in ASTM D5142-04 [28]. After the drying program was completed, the sample robot removed the crucible was immediately replaced on the sample arm in the furnace. This was an automated way of stirring the sample, very much like the biomass standard ASTM E1757-01 [29].

All TGA runs began with a 5 min isothermal hold at 110°C. This was implemented to ensure that the run began with a dry sample. The isothermal hold also ensured that the furnace was purged and that all samples started with identical temperature distributions and thermal equilibriums. All TGA runs ended with a rapid cool down from the maximum temperature to 110°C followed by a 3 min isothermal hold at 110°C. The weight at the end of this run was treated as the final weight of the run and used in all comparisons. The departure from and return to thermal equilibrium (110°C) mimicked the thermal conditions of a sample manually being placed in and removed from a furnace not equipped with a balance (e.g., the furnace specified by the ASTM D3174 and ASTM D3175 methods [30,31]).

Experiment 1: End Temperature Experiment—This experiment was performed to assess the changing "ash" content of manures at different end temperatures. The manures tested were the following: Swine flushed effluent, scraped dairy manure, and poultry litter. These samples were combusted under a zero-grade air atmosphere and flow rate of 80 $mL \cdot min^{-1}$ from 110°C to 150, 300, 450, 600, 750, or 900°C. The samples were subjected to a heating rate of $11°C \cdot min^{-1}$. This heating rate would allow the furnace to

TABLE 4—*Experimental conditions for tested TGA methods.*

Experiment	Purpose	Maximum Temperature (°C)	Ramp (°C/min)	Gas and Flow Rate (mL/min)	End Conditions	Total Run Time (min)
1	Ashing at varied temperatures	150, 300, 450, 600, 750, 900	11	Air,80	Hold 5 min	
2	Ashing at 600°C	600	11	Air,80	Hold 10 min	55
3	Traditional VM	950	200	N_2,80	Hold 7 min	24
	Traditional ash	(1) 750, (2) 950	(1) 11, (2) 3.5	Air,80	Hold at (2) 120 min	250
4	Modified VM	950	100	N_2,80	Hold 7 min	35
	Modified ash	950	11	Air,80	Hold 10 min	100

achieve 750°C within 60 min. Once the desired end temperature was achieved, the samples were held at temperature for 5 min, then cooled to 110°C ($-200°C \cdot min^{-1}$) before completing the run and obtaining the final weight measurement.

Experiment 2: 600°C *Ash Test*—The following samples were tested in triplicate ($n=3$) for their residue (ash) remaining after combustion at 600°C: Scraped dairy manure, poultry litter, swine flushed effluent, and swine sludge. The TGA-tested samples, exposed to a zero-grade air atmosphere (flow rate of 80 $mL \cdot min^{-1}$), were subjected to an $11°C \cdot min^{-1}$ heating rate with a 10 min isothermal hold at 600°C. The samples were cooled to 110°C at $-200°C \cdot min^{-1}$ for the 3 min isothermal hold before recording a final weight. The residue remaining was combusted again following the ASTM ash method described in the next section to determine the completeness of combusting the samples at 600°C.

Experiment 3: ASTM Method—All samples (Table 3) were tested for VM and ash content ($n=3$) following furnace conditions listed in ASTM D3175-07 and ASTM D3174-04 [30,31]. VM content was determined by subjecting samples to pyrolysis conditions—N_2 atmosphere at a flow rate of 80 $mL \cdot min^{-1}$—beginning at 110°C, and a $200°C \cdot min^{-1}$ ramp was implemented until the temperature reached 950°C. This temperature was held for 7 min. Then the sample was cooled before recording the final weight. The difference of the final weight and initial dry weight of sample served as the VM content. A single run for determining VM occurred within 24 min. The ash content was determined as the residue remaining after the following temperature program: $11°C \cdot min^{-1}$ increase from 110 to 750°C, $3.5°C \cdot min^{-1}$ increase until 950°C, isothermal hold at 950°C for 120 min, and rapid cooling to 110°C ($-200°C \cdot min^{-1}$). The ash method used zero-grade air at a flow rate of 80 $mL \cdot min^{-1}$. This method's elapsed time was a total of 250 min. The dry ash free VM (VM_{daf}) was determined based on the determined VM and ash contents for each respective method.

Experiment 4: Modified ASTM Method—The previous methods were modified slightly and used to determine the ash and VM ($n=3$) for the following samples: Scrapped dairy manure, poultry litter, swine flushed effluent, and swine sludge. Ash was determined with the following temperature program: $11°C \cdot min^{-1}$ increase from 110 to 950°C, 10 min isothermal hold at 950°C, and rapid cooling to 110°C ($-200°C \cdot min^{-1}$), followed by the isothermal 110°C hold. This modified method's elapsed time was less than half of the original method's time completing within 100 min. The ash method again used zero-grade air at a flow rate of 80 $mL \cdot min^{-1}$. The VM was determined as the matter removed from a dry sample under a N_2 flow rate of 80 $mL \cdot min^{-1}$ after the following temperature program: $100°C \cdot min^{-1}$ ramp from 110 to 950°C, 7 min 950°C isothermal hold, and $100°C \cdot min^{-1}$ cool down to 110°C. This modified method's time increased from 24 to 35 min. A tabular summary of these experimental conditions is presented along with the other experiments' conditions (Table 4).

Thermogravimetric Analysis Curve Processing and Statistics

Once the data were collected from the TGA, the data were stored in a database that was part of the StarE software suite. These data were transferred from the database to MATLAB v. 7.8 (R2009b) software (The MathWorks, Inc., Natick, MA). Routines written in MATLAB code were used to select final mass values used in all experiments.

FIG. 1—*Residue remaining from TGA combustion of swine, dairy, and poultry manures at different end temperatures (TGA method: 110–950°C; 11°C·min^{-1}; and zero-grade air 80 mL·min^{-1}).*

Statistical comparisons were made for the following results: Traditional ASTM standard procedure and TGA ASTM procedure (Exp. 3), traditional ASTM standard procedure and the modified TGA ASTM procedure (Exp. 4), and TGA ASTM procedure and the modified TGA ASTM procedure (Exp. 3 versus Exp. 4). Results were analyzed by Proc General Linear Model and least significant difference (LSD) with Version 9.2 of Statistical Analysis System (SAS Institute, Inc., Cary, NC). *F*-values were determined to be the mean square for the model divided by the mean square for the error. The *P*-value represented the significance probability associated with the *F*-value. If the model (e.g., VM is a function of method used) was considered significant at a *P*-value of <0.05, then the resulting VM or ash component was not the same among the methods tested. The LSD was defined to be the observed difference between two sample means necessary to declare the population means different [32].

Discussion

The observation of the residues remaining after each end temperature tested in Exp. 1, as presented in Fig. 1, indicated that as combustion reached higher temperatures, the samples exhibited both colorimetric and geometric changes. The residues changed from a black color, indicating devolatilization [23,33], to orange shaded residues. This orange shade was likely due to the oxidation of iron and other minerals commonly found in the ash portion of animal manures [34,35]. The residues were loosely packed into the crucibles, and as temperatures increased, they became cylindrical in shape, diminishing in size. The TGA of the combusted manure samples in Fig. 2 suggested that temperatures greater than 600°C would be necessary to remove all available VM and FC. This was also confirmed by the visual inspection of the residues at 600 and 750°C; the 750°C residues appeared smaller in diameter.

When isothermal hold at 600°C increased from 5 to 10 min (from Exp. 1 to Exp. 2), the ash contents of the swine, dairy, and poultry manures determined by the TGA were slightly greater than those determined by the traditional method (Table 5). Subjecting the ashed TGA samples to the temperature profile in the ASTM standard ash method (ASTM D3174-04) resulted in 0.40–9.40 wt%$_{db}$ weight loss of the original sample weight. Thus, the combustion at 600°C for 10 min did not completely remove all VM and FC. This was true especially in the case of flushed swine effluent. During a reburn of this manure, the mass removed from the original sample was 9.40 wt%$_{db}$.

ASTM Methods

In order to determine the number of replications necessary to achieve an adequate representation of a population, the VM content of swine lagoon sludge was determined via TGA methods for 30 random samples. From these 30 samples representing a population, groups of 2, 3, 4, 5, 7, 10, 15, 20, and 25 samples were randomly selected, and their sample means and standard deviations (SDs) were calculated. Figure 3 shows that as few as two replications produced the sample means within one SD of the population mean. Albeit small size samples (milligram ranges in TGA), the well grounded and homogenized manure samples in our procedure were homogeneous enough, in combination with efforts to reduce effects of environmental noise, that duplicate or triplicate TGA results should adequately represent the population.

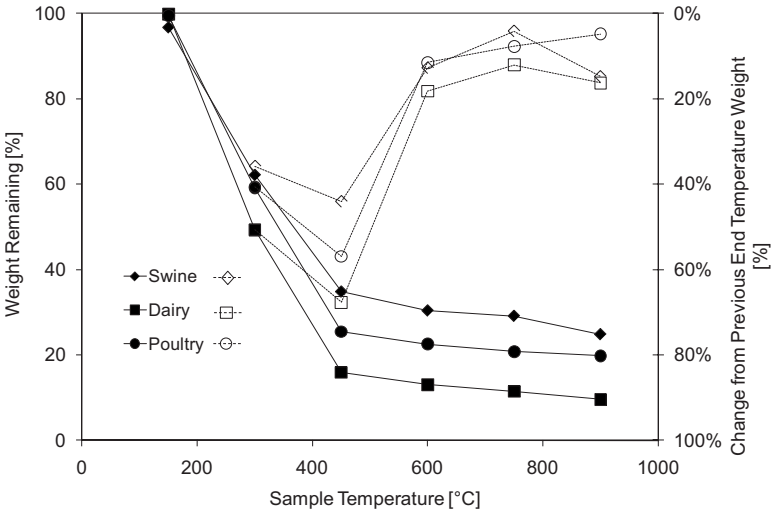

FIG. 2—*TGA of remaining residue from combustion of swine, dairy, and poultry manures at end temperatures of 150, 300, 450, 600, 750, and 900°C (closed symbols = weight remaining; open symbols = change from previous end temperature weight; TGA method: 110–950°C; 11°C·min^{-1}; zero-grade air 80 mL·min^{-1}).*

TABLE 5—*Comparison of ash results (wt%$_{db}$) for animal manures between traditional and TGA determined ash methods at 600°C (n = 3; traditional method: ASTM D3174-04; TGA$_{600}$ method: 80 mL·min^{-1} zero-grade air; 110–600°C; 11°C·min^{-1}; 10 min 600°C isothermal hold).*

		Traditional		TGA_{600}		
Manure	Description	Mean	SD[a]	Mean	SD	Reburn Weight Loss[b]
Swine	Flushed effluent	31.92	0.73	33.41	1.23	9.40
	Sludge	46.90	0.74	48.56	3.69	4.80
Dairy	Scraped influent	13.75	1.19	17.00	3.91	3.69
Poultry	Soiled litter	22.29	0.05	24.76	1.04	0.40

[a]SD = standard deviations.

[b]wt% based on original sample weight.

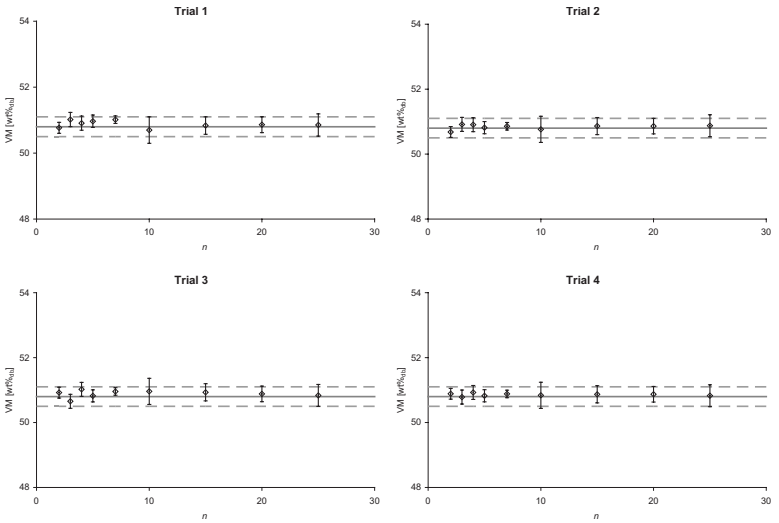

FIG. 3—*Sample means and SD of multi-replication results for TGA determination of VM in swine sludge for group samples of n = 2, 3, 4, 5, 7, 10, 15, 20, and 25 (TGA method: 80 mL·min^{-1} N_2; ASTM D3175-07).*

TABLE 6—*Statistical summary table for traditional and TGA determinations of dry ash free VM content (wt%$_{daf}$) in tested animal manures.*

		Traditional			TGA					
Manure	Description	Mean	*n*	SD[a]	Mean	*n*	SD	LSD[b]	*F*-Value	*P*-Value
Swine	Flushed influent	89.86[c]	1	⋯	84.96	3	3.18	6.08	1.78	0.314
	Separated solids	90.07[c]	3	1.57	86.14	3	4.61	3.93	1.96	0.234
	Sludge	88.84[c]	6	0.93	88.98	6	1.18	3.15	0.05	0.823
Dairy	Scraped influent	79.97[c]	3	1.23	79.95	3	2.02	3.93	0.00	0.991
	Separated solids	81.32[c]	3	0.86	80.31	3	0.84	3.93	2.13	0.218
Poultry litter	Soiled litter	78.83[c]	3	7.91	80.39	3	3.73	3.93	0.10	0.773
Rabbit	Manure pellet	⋯		⋯	76.03	3	2.12	⋯	⋯	⋯
	Compost (3-4 years)	⋯		⋯	83.67	3	4.31	⋯	⋯	⋯

[a]SD=standard deviation.

[b]LSD between methods based on $\alpha=0.05$.

[c]Values within a method followed by the same letter are not considered statistically different (traditional: df=15, MSE=9.301, and critical t =2.131; TGA: df=19, MSE=8.066, and critical t=2.093).

The values reported for both VM and ash were within expectations with VM ranging between 47 and 78 wt%$_{db}$ and ash ranging between 4 and 47 wt%$_{db}$ [10]. Within the traditional methods, the VM$_{daf}$ values (Table 6) within an animal group were considered similar (i.e., all swine samples were considered similar to one another yet different from all dairy samples, which were similar to one another). When the TGA method was used, multiple differences were noted among the different animal manures; however, no discernable pattern or grouping could be formulated (e.g., raw poultry litter VM$_{daf}$ values were similar to the swine flushed influent, all rabbit, and all dairy, manures; however, swine influent and dairy influent were considered statistically different). A discussion covering why there are differences within animal manure groups as well as the effects of waste treatment on ash is beyond this study's scope. However for this study, VM and ash contents among all manure samples were not different between traditional and TGA ASTM determined methods. In fact, there was an almost linear relationship between the two methods' results (Fig. 4). Statistical analysis of these two methods' VM results (excluding the rabbit manures) yielded a LSD value of 3.02 wt%$_{db}$. As such, traditional and TGA method results for VM were considered similar: VM content using traditional methods averaged 61.88 wt%$_{db}$ (n=95) compared to TGA determined content of 62.58 wt%$_{db}$ (n=105). The same outcome was true for the ash content calculated for all tested samples; this included the rabbit manure. Analysis predicted a LSD value of 3.69 wt%$_{db}$ with traditional method determined ash content averaging 26.03 wt%$_{db}$ (n=125) and TGA determined ash averaging 26.42 wt%$_{db}$ (n=135).

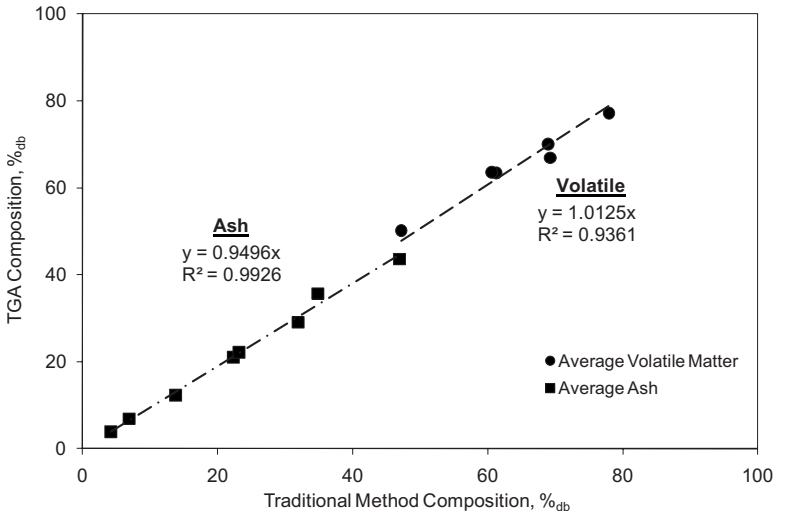

FIG. 4—*Comparison of traditional and TGA determined VM and ash content (%$_{db}$) following ASTM D3175-07 and ASTM D3174-04, respectively, of various animal manures (perfect method agreement would have a slope of 1; TGA method: N_2 or zero-grade air flow rate of 80 mL·min^{-1}).*

TABLE 7—*Statistical summary table for traditional and TGA determinations of VM content ($wt\%_{db}$) in animal manures following ASTM D3175-07 (TGA method: N_2 flow rate of 80 $mL \cdot min^{-1}$).*

		Traditional			TGA					
Manure	Description	Mean	*n*	SD[a]	Mean	*n*	SD	LSD[b]	*F*-Value	*P*-Value
Swine	Flushed influent	60.60	1	···	63.56	3	1.01	5.02	6.41	0.127
	Separated solids	69.21	3	1.14	66.92	3	1.29	2.76	5.28	0.083
	Sludge	47.17	6	0.21	50.18	6	0.94	0.88	58.71	0.000
Dairy	Scraped influent	68.96	3	0.20	70.06	3	0.44	0.78	15.28	0.017
	Separated solids	77.93	3	1.07	77.19	3	1.42	2.85	0.51	0.515
Poultry litter	Soiled litter	61.26	3	6.15	63.45	3	1.90	10.32	0.35	0.587
Rabbit	Manure pellets	···		···	70.79	3	2.35	···	···	···
	Compost (3-4 years)	···		···	53.82	3	2.74	···	···	···

[a]SD=standard deviation.
[b]LSD based on $\alpha = 0.05$.

Once individual sample results between the methods were compared, statistical similarities were noted for most VM and ash contents (*P*-value of >0.05; Tables 7 and 8). However, there were notable statistical differences (*P*-value of <0.05) in the VM contents of both dairy scraped influent and swine anaerobic lagoon sludge. For the dairy scraped influent, the traditional method determined a lower VM content—68.96 versus 70.06 $wt\%_{db}$. For swine sludge, the traditional method also yielded a lesser VM content—47.17 compared to 50.18 $wt\%_{db}$. However, the traditional methods predicted a greater ash content of the sludge—46.90 versus 43.60 $wt\%_{db}$. These differences in the sludge samples may be attributed to the sludge's high ash content. This estimated ash content was the greatest in this study. Since the traditional ash method oxidized the sludge at 600°C, this temperature, despite the 120 min isothermal hold, may not have been high enough to remove all combustible materials (VM and FC). This explanation as to why the TGA predicted numerically greater ash contents than traditional non-instrumental methods is further supported by the previous 600°C TGA results as well as the multi-replication experiment. The traditional VM and ash methods also required gram-size samples versus the milligram samples used in the TGA methods. With the gram-size sample (combined with the swine sludge's high ash content), there could have been the occurrence of heat transfer limitations. These limitations would not allow the complete devolatilization or oxidation of the material at the center of the sample. One way to overcome this in non-automated methods would be to require an additional mid-run mixing or shaking step. In contrast, the TGA methods using milligram-size samples allowed for a more uniform distribution of heat transfer and effectively devolatilized and oxidized the material in the center of the cylindrical residues. Therefore, TGA method with many smaller samples sizes (milligram versus gram ranges) should produce more accurate results with respect to VM and ash; this would be true as long as the samples are adequately homogenized as in our procedure. As a consequence of small sample size, ash content results appeared to be less precise (i.e., greater SDs). Thus, numerically small differences in mass loss greatly affected replicated ash and VM values. In order

TABLE 8—*Statistical summary table for traditional and TGA determinations of ash content ($wt\%_{db}$) in animal manures following ASTM D3174-04 (TGA method: Zero-grade air flow rate of 80 $mL \cdot min^{-1}$).*

		Traditional			TGA					
Manure	Description	Mean	*n*	SD[a]	Mean	*n*	SD	LSD[b]	*F*-Value	*P*-Value
Swine	Flushed influent	31.92	3	0.73	29.04	3	1.90	3.96	4.08	0.113
	Separated solids	23.16	3	0.13	22.19	3	3.39	5.44	0.25	0.646
	Sludge	46.90	6	0.74	43.60	6	0.57	0.85	74.58	0.000
Dairy	Scraped influent	13.75	3	1.19	12.34	3	1.87	3.55	1.22	0.331
	Separated solids	4.18	3	0.79	3.89	3	1.00	2.05	0.15	0.714
Poultry litter	Soiled litter	22.29	3	0.05	21.03	3	1.34	2.15	2.65	0.179
Rabbit	Manure pellet	6.89	2	0.16	6.88	3	2.16	5.12	0.00	0.997
	Compost (3-4 years)	34.81	2	0.36	35.67	3	1.30	3.13	0.77	0.445

[a]SD=standard deviation.
[b]LSD based on $\alpha = 0.05$.

TABLE 9—*Statistical summary table for traditional, standard TGA, and modified TGA determination of VM content ($wt\%_{db}$) in animal manures (traditional: ASTM D3175-07; standard TGA method: 80 mL·min^{-1} N_2; ASTM D3175-07; modified TGA method: 80 mL·min^{-1} N_2; 110–950°C; 100°C·min^{-1}; 7 min 950 °C isothermal hold).*

		Traditional	Standard	Modified				
Manure	Description	Mean[a]	Mean[a]	Mean	SD	LSD[b]	*F*-Value	*P*-Value
Swine	Flushed influent	60.60[c]	63.56	65.83	9.97	50.19[d]	0.22	0.811
	Sludge	47.17	49.45	49.12	2.64	3.12	2.01	0.215
Dairy	Scraped influent	68.96	70.06	65.21	1.61	1.94	20.64	0.002
Poultry litter	Soiled litter	61.26	63.45	63.80	0.17	7.42	0.41	0.680

[a]SD presented in Table 7.

[b]LSD based on $\alpha = 0.05$, $t = 2.447$, and df = 6.

[c]$n = 1$.

[d]Mean square error reported: $t = 2.776$ and df = 4.

to increase the precision of the TGA method (i.e., reduce the SD), an individual testing laboratory performing routine TGA analysis could establish a procedural protocol that included information for an acceptable number of replications and sample weight range.

With most sample TGA results being in agreement with the results from traditional ASTM methods, modifications to the TGA method were implemented to assess (1) whether sufficient time was allowed for complete devolatilization and (2) whether a shorter 950°C isothermal hold yielded similar ash results. For all samples except for the dairy scraped influent, increasing the time for devolatilization to occur produced results similar to both the traditional method and the standard TGA method (Table 9). This suggested that the 7 min isothermal hold at 950°C was sufficient for determining the VM contents of manures. For the dairy scraped manure, other methods should be investigated, which modify the temperature profiles. Fortunately, for the modified TGA ash method, the shorter isothermal 950°C hold did not alter the final ash content (Table 10). In all cases examined, the modified TGA method ash values were the same as the standard TGA ash method values. Just like the difference noted in the standard TGA method with the traditional method for swine sludge ash, the modified TGA ash method differed from the traditional ash method value—43.82 versus 46.90 $wt\%_{db}$. This could be explained with the same reasoning detailed earlier. Therefore, the modified TGA ash method can be implemented and effectively determine the ash content of manures.

Summary

After a review of available ASTM standards and methods for determination of VM and ash content in various biomass and materials, an investigation was conducted to address the use of instrumental TGA techniques for the quantification of VM and ash in various animal manures. The TGA methods applied followed the temperature profile in the traditional ASTM methods. Modifications to these methods were also implemented and compared against non-instrumental results as well as the standard TGA method. The following is a summary of our findings.

TABLE 10—*Statistical summary table for traditional, standard TGA, and modified TGA method determinations of ash content ($wt\%_{db}$) in animal manures (traditional: ASTM D3174-04; standard TGA method: 80 mL·min^{-1} zero-grade air; ASTM D3174-04; modified TGA method: 80 mL·min^{-1} zero-grade air; 110–950°C; 11°C·min^{-1}; 10 min 950°C isothermal hold).*

		Traditional	Standard	Modified				
Manure	Description	Mean[a]	Mean[a]	Mean	SD	LSD[b]	*F*-Value	*P*-Value
Swine	Flushed influent	31.92	29.04	30.64	1.74	3.48	2.05	0.209
	Sludge	46.90	43.13	43.82	0.45	1.06	43.79	0.0003
Dairy	Scraped influent	13.75	12.34	11.66	5.35	6.67	0.31	0.528
Poultry litter	Soiled litter	22.29	21.03	21.07	2.17	2.94	0.71	0.747

[a]SD presented in Table 8.

[b]LSD based on $\alpha = 0.05$, $t = 2.447$, and df = 6.

(1) TGA methods for the evaluation of VM and ash in animal manures were the same as those values found through non-automated ASTM standards.
(2) TGA techniques offered a more complete oxidation and devolatilization of manure samples, especially those with greater ash content, due to the small sample size that is amenable to uniform temperature distributions. However, the precision of TGA values would need to be improved by more replications and established sample loading methods.
(3) The TGA determination of VM in manure should follow ASTM D3175-07. This requires the flow rate of N_2 is between two and four furnace exchanges per minute.
(4) The TGA determination of ash in manure should occur above 600°C with preference for the following method: Zero-grade air at 80 $mL \cdot min^{-1}$, heating rate of $11\,°C \cdot min^{-1}$, temperature range of 110–950°C, and isothermal hold at 950°C for 10 min.

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