

METHODS FOR MEASURING MOISTURE CONTENT OF GRAINS AND IMPLICATIONS FOR RESEARCH AND INDUSTRY

Fred Owens and Steve Soderlund
Pioneer Hi-Bred, A DuPont Business
Fred.Owens@Pioneer.com



ABSTRACT

Several methods were used to measure “weight loss on drying” and moisture content of 120 samples freshly harvested corn grain containing from 12 to 45% moisture (10 different hybrids; 6 harvest dates; grain separated from the butt and tip section of multiple ears). Moisture content varied with measurement method. Compared with direct measurement of water content by a chemical reaction (the Karl Fischer method), drying whole kernel corn samples for 144 h at 62 C failed to remove approximately 3% of the water, especially from drier samples. Weight loss during oven drying at 105 C for 144 h matched Karl Fischer estimates of moisture content very closely. Rapid moisture measurements by near infrared procedures were almost as accurate as 105 C drying. Capacitance-conductance measurements were slightly less accurate than 105 C estimates, particularly for samples that contained more moisture. Compared with moisture content of kernels obtained from the tip half of the ear, kernels from the butt half of the ear contained up to 5% more moisture. Compared with the samples tested, weight loss on drying would be greater from samples that contain volatile compounds derived from microbial fermentation (high moisture corn; silage; wet distillers grains). For such samples, more accurate prediction of caloric value would be obtained by measuring volatiles and water content separately by appropriate procedures. If properly calibrated, near infrared techniques hold promise for obtaining such measurements.

INTRODUCTION

Moisture content of a feed usually is calculated as the weight lost by material during application of heat to a sample. Indeed, Thiex and Richardson (2003) proposed that the term “weight loss on drying” should be substituted for the term “moisture” when discussing feeds. Hence, the term “dry matter” probably should be replaced with “100 minus weight loss on drying.” This revised terminology is based primarily on the observation that numerous compounds (organic acids, ethanol, ammonia) in addition to water become volatile and are lost when a feed is heated. But in addition, heating can result in chemical reactions that release water. Of primary concern in the grain trade is the loss of volatile compounds during drying of certain feedstuffs, e.g., silages, high moisture corn, wet distillers products. Loss of volatiles results in an underestimate of dry matter content of the feedstuff; in turn, this inflates the efficiency of feed use (gain to fed dry matter ratio) as an estimate of the true energetic efficiency of fermented crops and wet distillers products. If weight lost during fermentation is combined with the improved gain to feed dry matter ratio, these two errors will partially cancel, but very seldom are these two measurements both measured and combined. Consequently, if one inhibits fermentation so that a fermented product contains a lower concentration of volatile compounds, dry matter recovery increases.

Further, apparent digestibility increases because the dry matter fed has fewer volatile compounds that are lost during drying. Perkins (1943) noted that 4 to 7% more dry matter was lost from corn silage by 100 C drying than by toluene distillation. Fox and Fenderson (1978) found that try DM of corn silage was underestimated by 8% and 11% by oven drying at 60 and 100 C, respectively.

As discussed by Thiex and Richardson (2003), chemical water content should be measured by the Karl Fischer titration method. By this procedure, the extent of a chemical reaction quantifies the amount of water present. Being considerably more complex, time-consuming, and expensive than drying samples with a forced air, vacuum, or microwave oven, the Karl Fischer titration seldom is used for routine measurement of moisture content. However, even the standard operating procedures for moisture measurement by oven drying will vary with feed type and among laboratories. Standard procedures include vacuum oven drying at 95 to 100 C (AOAC 934.01), forced air oven drying at 103-104 C for 5 h (AOAC 935.29), drying at 135 C for 2 h (AOAC 930.15), and 105 C for 3 h (NFTA 2.2.2.5). Drying samples above 65 C without aeration for rapid removal of moisture will cause formation of Maillard products that will be assayed erroneously as lignin (Van Soest, 1982). As a result, some laboratories use a two-stage procedure; to

obtain a sample for chemical analysis, the sample is first dried at a lower temperature. A sub-sample then is dried further drive off any remaining moisture. Assay results are converted to a dry matter basis based on the additional weight lost during drying at the higher temperature. Some laboratories substitute near infrared reflectance or transmission (NIR/T) procedures for the high temperature drying. Methods for determining the nutrient content of dried distillers products were compared recently. Drying at 135 C overestimated the moisture content of distillers products determined by the Karl Fischer procedure, so a lower drying temperature (105 C for 3 h) currently is recommended (AFIA, 2007). Whether the additional weight lost at the higher temperature is due to loss of additional volatile compounds present in the product or to formation of complexes (e.g., Maillard products) that result from rearrangement of sugars that dehydrate when condensing with amines is not certain. One additional procedure that was popular in the past for silage, toluene extraction, is an awkward and inefficient process and may extract some volatiles, as well. However, the toluene distillation procedure proved more “accurate” than freeze drying or oven drying at 70C or 100C for high moisture roughages and feces in one report (Aerts et al., 1974). Because of its speed, microwave oven drying is a preferred sample drying method at many analytical laboratories. Uneven microwave heating can cause charring of samples that interferes with subsequent spectral measurements and perhaps with wet chemistry assays, as well.

Indirect measurements that do not involve removal of water also are used to quantify the amount of water present in a sample. Approved as an official method for determining the moisture content of grain, electrical conductivity tests are used widely to determine the moisture content of unfermented grain, but for fermented grains or feeds and for feeds with acids added (e.g., propionic acid as a preservative), electrical conductivity is increased by the acids leading to an overestimate of moisture content. Thus, harvested grains should not be allowed to ferment prior to electrical conductivity measurements. Nevertheless, for measuring the moisture content of harvested but unfermented grain, conductivity meters cross-checked by oven drying of similar samples are used routinely due to their very rapid sample throughput.

Near infrared reflectance or transmission also is a rapid, officially sanctioned method for determining moisture content of grains. Unfortunately, the standards employed for calibrating NIR/T measurements often are not specified clearly. When calibrated against moisture measured by oven drying fermented samples, volatiles would be considered water, but if the calibration set consists of samples where reference samples were either devoid of volatiles or where moisture was measured by Karl Fischer procedures, volatiles will not be equated with dry matter. In the latter cases, the wavelengths selected for moisture measurement should be related only to “true” water. In this case, NIR/T measurements, perhaps inadvertently, would properly quantify the true moisture content of feeds even when volatiles are present. Small RF-impedance or microwave shift devices also have been devised to measure moisture content of single corn kernels; these may prove useful in the field to check moisture content at harvest.

Considering the myriad of dry matter procedures currently being used, what analytical methods are preferred and what impact would a change in method have on research findings and feed formulation? From a chemist’s viewpoint, equating volatile compounds with water is wrong. Quantifying water and volatile compounds separately would be preferred. However, in the grain trade, those who sell and those who buy grain need to agree on specific assay methods both for dry matter and other assayed constituents. With fermented feeds being routinely traded on a dry matter basis, equating volatiles with water favors the buyer. In contrast, chemically measured water content that excludes volatiles would favor the seller. Most published research information relating to nutritional value of feeds has been determined by oven drying at 105 C. Consequently, switching to chemically determined water would abruptly reduce the apparent feeding value of dry matter from feeds containing volatile compounds. Unfortunately, the relative quantity of volatiles present in a feed can vary with processing procedures and the extent of fermentation, so the degree of error involved with moisture measurement will vary.

MATERIALS AND METHODS

To examine the relative difference in absolute estimates of moisture content and repeatability of various moisture measurement methods, high

moisture corn was harvested from 10 different hybrids grown at a single location at 6 different stages of maturity ranging from 12 to 45% moisture (55 to 88%) dry matter. Ears were split in half; kernels from the tip section of each of 6 ears were shelled and combined to form a sample. Similarly, samples of the butt fraction of ears were combined to form a sample. This resulted in 120 samples (10 hybrids; 6 dates; tip versus butt) of whole kernel corn that were assayed for weight loss when dried in forced-draft ovens maintained at 62C or 105C for 144 hours (to assure full removal of heat volatile substances), capacitance-conductance using a GAC (GAC 2100; Dickey-John Corporation, Auburn, IL), near infra-red transmission with a Foss instrument (FOSS 6500; FOSS NIR Systems, Inc., Laurel, MD), and Karl Fischer titration at a commercial laboratory (Servi-Tech, Dodge City, KS). In addition, vacuum oven drying at 105 C for 24 h and 135 C for 8 h was tested initially, but testing by these procedures was discontinued due to extensive condensation inside the vacuum chamber and sample charring problems, respectively. Note that these high moisture corn grain samples were not fermented. Consequently, concentrations of organic acids and alcohols from fermentation would be virtually nil. Instead, these samples should be most similar to harvested high moisture corn delivered fresh to a location for storage. The Karl Fischer titration measurement, being chemically measured water

content, was considered the “Gold Standard” (Thiex and Richardson, 2003); moisture content (weight loss) from other assays was compared to moisture determined by the Karl Fischer titration procedure.

RESULTS AND DISCUSSION

Drying in a forced draft oven at 62 C to a constant weight resulted in less weight loss than drying at 105 C (Figures 1 and 2). Despite a high correlation ($R^2 > 0.99$) between weight loss at 62 C and Karl Fischer moisture content, 2 to 4% chemically determined moisture remained in samples following 144 hours in the forced draft oven at 62C; the difference was slightly greater with drier samples. One would expect that drying to a constant weight at any temperature and even freeze-drying should result in loss of similar amounts of water if such processes remove all free water. Whether lower weight loss associated with the cooler drying temperature is due to residual moisture retained by or bound to specific feed components (e.g., protein, starch, or minerals), to formation of cross-links among monomers resulting in complexes that inhibit release of water, or to disruption of particles, e.g., starch granules, with internalized water by the elevated temperature or released during Fischer titration is uncertain. Though unlikely, the Karl Fischer chemical procedure might react with components in feeds in addition to water.

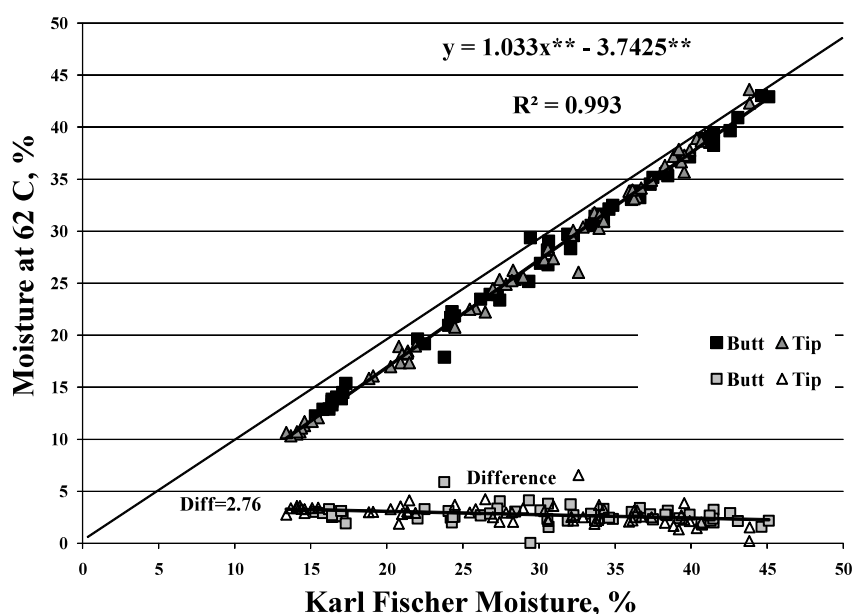


Figure 1. Comparison of weight loss during exposure at 62 C for 144 h to Karl Fischer titrated moisture content of high moisture harvested corn grain.

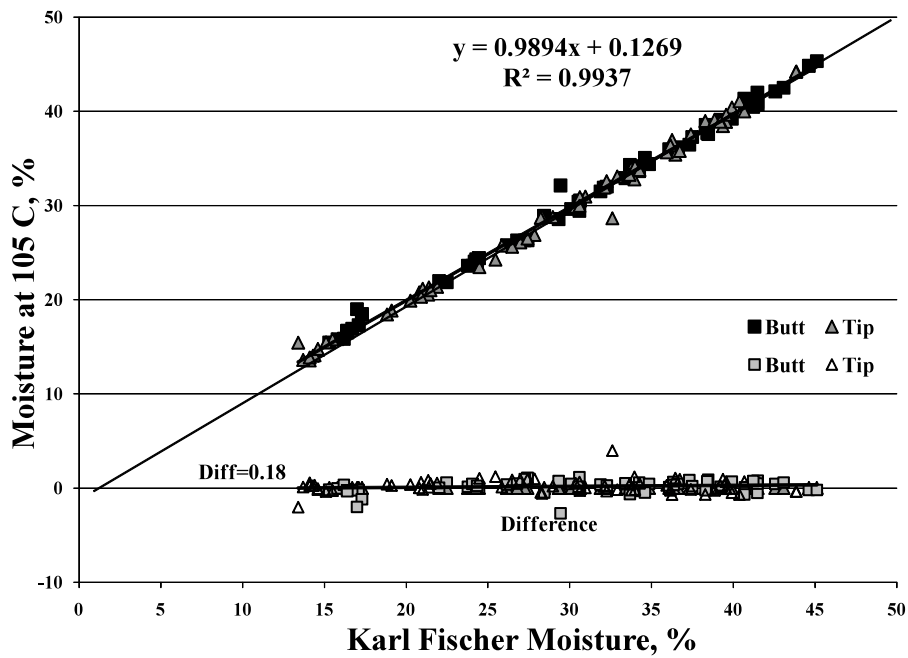


Figure 2. Weight loss at 105 C versus Karl Fischer titrated moisture measurements for 120 high moisture corn grain samples.

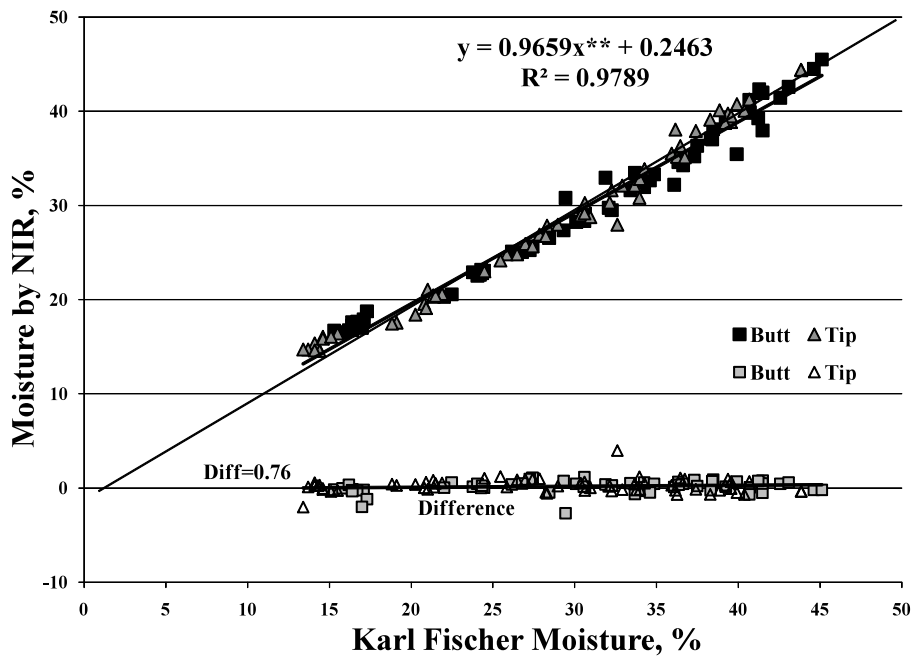


Figure 3. Moisture content estimated by near infrared transmission procedures (FOSS 6500).

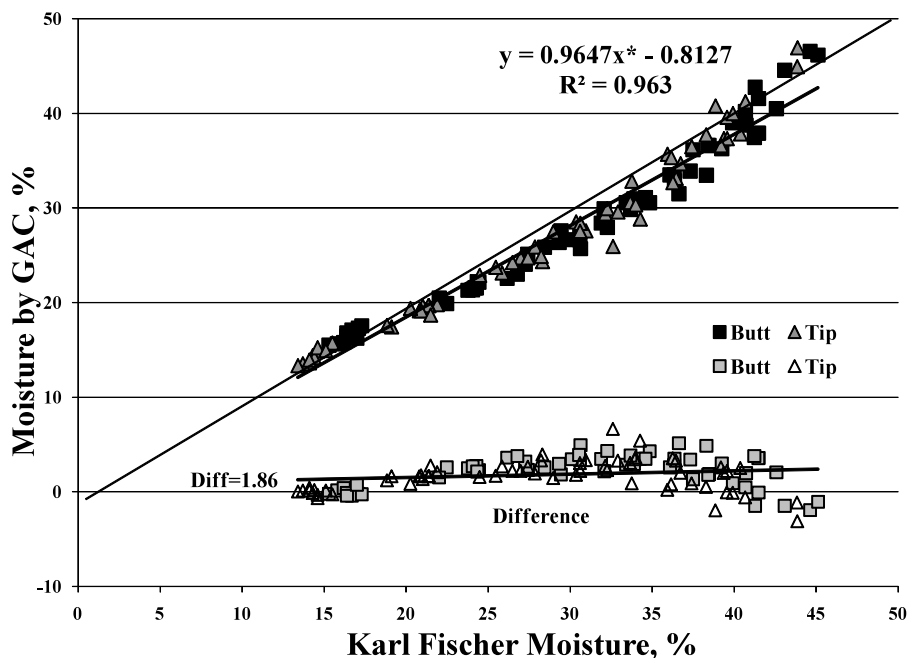


Figure 4. Comparison of capacitance-conductance estimates of moisture content with a Dickey-John GAC 2100 versus Karl Fischer titration moisture measurements for 120 samples of high moisture corn grain.

Drying at 105 C for 144 hours resulted in weight loss equivalent to water content measured by Fischer titration (Figure 2). The NIT instrument (Figure 3) and the capacitance-conductance instrument (Figure 4), presumably because both were calibrated against moisture loss by oven drying of grain, resulted in similar accuracy and precision with little apparent bias in estimated water content relative to Fischer titration. Whether an NIT instrument calibrated for unfermented grains could accurately measure the Karl Fischer moisture content of fermented grain that contains additional volatile substances was not determined in this study. Certainly, to determine the moisture content devoid of volatiles, calibration samples used for fermented grain should be based either on Fischer titration or oven drying of grain PRIOR to fermentation. Calibrated in this fashion, moisture content would be lower than when estimated by oven drying.

Moisture content of grain from different sections (tip vs butt) of the ear of corn freshly removed from the corn plant differed in moisture content. Kernels from the butt typically had 2 to 5% more moisture content whether estimated by weight loss during drying or by Fischer titration (Figure 5). This

difference in moisture content between kernels from the tip and the butt was greater for corn hybrids with tighter husks and upright ears. Additional factors associated with rate of field drying of grain were outlined by Nielsen (2002). A wide variation among kernels in moisture content could result in mold problems during aerobic grain storage due to high moisture content of wet kernels (Bonifacio-Maghirang et al., 1997). Moisture content of individual kernels is of particular concern if moisture does not migrate among kernels when grain is stored. Moisture migration among intact corn kernels appears limited. In one elegant study from Illinois, a single batch of grain was formed by blending two batches of whole corn that differed in mean moisture content. The difference in moisture content between individual wet and dry kernels persisted during the several weeks that this grain resided in holds on ships while being transported to Japan! Consequently, mean moisture content may be incomplete as a measure of mold resistance of individual kernels of grain within a blend from various sources. Rolling and grinding the grain into storage with or without addition of water should aid moisture migration among grains that differ in moisture content.

This variation in moisture content of individual kernels indicates that when moisture estimated with devices that assay individual kernels may prove imprecise unless that measurement is averaged across multiple kernels from different locations on the ear or within a blended batch of grain. The range in moisture content among individual kernels should be greater for blended grain than for single hybrids grown in a single environment, particularly if some grain in the blend has been heat dried and other grain within the blend was dry at harvest. Such genetic and environmental differences can markedly complicate grain processing (particularly grinding and flaking) and result in an inconsistent product. Consequently, batches of grain delivered from storage from a single farmer should result in more consistent product for processing than blended commercial grain. However, grain farmers usually spread their risk of plant

diseases by planting multiple hybrids; if the multiple hybrids selected by a grain farmer are similar in seed size, texture, and composition, the blended grain should be more consistent for processing. Among processing methods, high moisture corn should have a marked advantage because 1) grain typically is obtained from a limited distance and thereby should have a similar environmental history and potentially a similar genetic history, and 2) multiple sources of grain are not processed individually but are blended both into and out of storage leading to a more consistent product for feeding. As compared with whole grain, any processing method that decreases particle size and blends particles should increase the uniformity of the final mixture unless over-mixing or feed handling permits particles to segregate based on density or particle size.

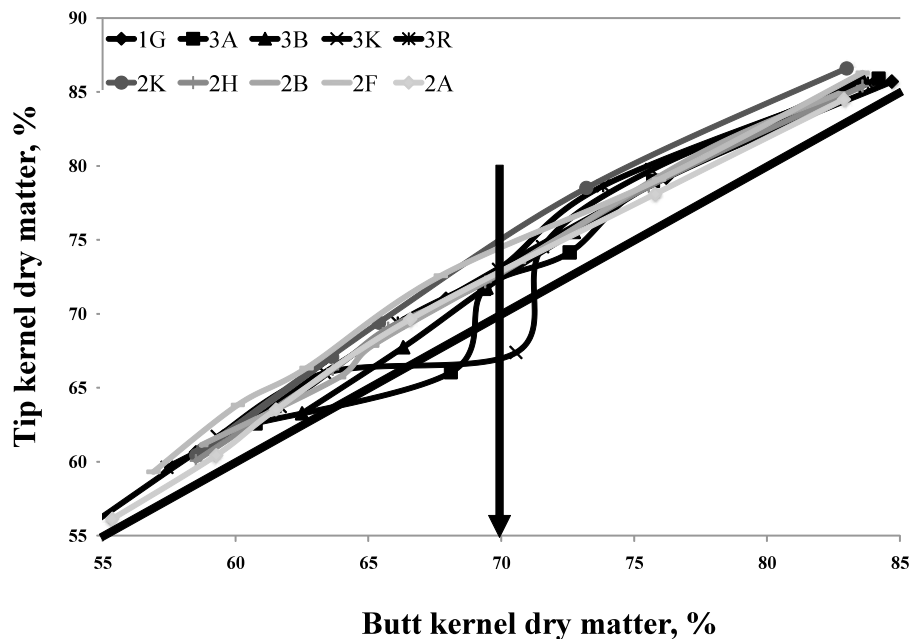


Figure 5. Moisture content based on Karl Fischer titration measurements for kernels from the tip and the butt section of ears of corn from 10 different hybrids.

IMPLICATIONS

Though considered to be a simple assay procedure, moisture content of a feed will vary with the specific measurement procedure used. Weight loss during oven drying at 105 C for 144 h matched chemical (Karl Fischer) estimates of moisture content for unfermented whole corn kernels very closely. Rapid moisture measurements by near infra-red

procedures proved almost as accurate as 105 C drying; capacitance-conductance measurements were only slightly less accurate than 105 C estimates for these unfermented grain samples. Ideally, for feeds containing volatile substances, “true” water and volatile compounds should be measured separately. But abruptly switching from measuring moisture content as “weight loss on drying” to direct

measurement of “true” water would disrupt scientific research and the grain trade that currently base moisture content on “weight loss during drying.” For

buying and selling grain, parties must agree on the analytical procedures to be used regardless of its precision and accuracy.

LITERATURE CITED

- Aerts, J. V., D. L. De Brabander, B. G. Cottyn, F. X. Buysse, R. J. Moermans. 1974. Comparison of methods for dry matter determination of high moisture roughages and faeces. *J. Sci. Food Agric.* 25:619-627.
- AFIA. 2007. Evaluation of analytical methods for analysis of dried distillers grains plus solubles. http://www.afia.org/img/assets/1176/DDGS_.pdf?DDGS+.pdf.
- Bonifacio-Maghirang, E.B., M. R. Paulsen, M.R., L. D. Hill, L.D., and K. L. Bender, K.L. 1997. Single kernel moisture variation and fungal growth of blended corn. *Applied Engineering in Agriculture* 13(1):81-89. <http://eru.gmpc.ksu.edu/publications/documents/SingleKernelEBM.pdf>.
- Fox, D. G., and C. L. Fenderson. 1978. Influence of NPN treatment, oven temperature, and drying time on error in determining true corn silage dry matter. *J. Anim. Sci.* 47:1152-1156.
- Nielsen, R. L. 2002. Grain drydown in the field after maturation. Corny News Network, Purdue University. http://www.agry.purdue.edu/ext/corn/news/articles.02/Grain_Drydown-0911.html.
- Perkins, A. E. 1943. Dry matter determination in green plant material and in silage. *J. Dairy Sci.* 26:545-551.
- Thiex, N, and C. R. Richardson. 2003. Challenges in measuring moisture content of feeds. *J. Anim. Sci.* 81:3255-3266.
- Van Soest, P. J. 1982. *The Ruminant Animal*. O & B Books, Corvallis, OR. pp. 130-131.