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Original Research

Comparison of Near Infrared Reflectance Spectroscopy and Raman Spectroscopy for Predicting Botanical Composition of Cattle Diets☆

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ABSTRACT

Diet selection is an important driver of ecosystem structure and function that is difficult to measure. New spectroscopic instruments are available for evaluating their applicability to ecological field studies. The objective of this study was to compare near-infrared reflectance spectroscopy (NIRS) to Raman spectroscopy of fecal samples for predicting the percentage of honey mesquite *(Prosopis glandulosa)* in the diet of ruminally fistulated cattle fed three different hay diets and compare them for their ability to discriminate among the three base diets. Spectra were collected from feces from a feeding trial with mesquite fed at 0%, 1%, 3%, and 5% of the diet and base hay diets of timothy hay *(Phleum pratense)*, Sudan hay *(Sorghum sudanense)*, or a 50:50 combination of Bermudagrass hay *(Cynodon dactylon)* and beardless wheat hay *(Triticum aestivum)*. NIRS and Raman spectra were used for partial least squares regression calibrations with the timothy and Sudan hays and validated with the Bermudagrass/beardless wheat hay diets. NIRS spectra provided useful calibrations ($r^2 = 0.88$, slope = 1.03, intercept = 1.88, root mean square error = 2.09, bias = 1.95, ratio of performance to deviation = 2.6), but Raman spectra did not. Stepwise discriminant analysis was used to select wavenumbers for discriminating among the hays. Fifteen of 350 possible wavenumbers for NIRS spectra and 29 of 300 possible wavenumbers for Raman spectra met the $P \leq 0.05$ entry and staying criteria. Canonical discriminant analysis using these wavenumbers resulted in 100% correct classification for all three base diets, and the Raman spectra provided greater separation than NIRS spectra. Discrimination using Raman spectra was primarily associated with wavenumbers associated with undigestible constituents of the diet (lignin). In contrast, discrimination using fecal NIRS (f.NIRS) spectra was primarily associated with wavenumbers associated with digestible constituents in the diet (protein, starch, and lipid). We believe that Raman spectroscopy deserves further investigation as a quantitative technique in ecological field studies.

Introduction

Honey mesquite (*Prosopis glandulosa* Torr.) is an invasive shrub that is common in the southwestern United States and northern Mexico. The leaves of honey mesquite have forage quality characteristics similar to moderate quality hay, with crude protein levels of 12—20% and neutral detergent fiber levels of 35—40% (Baptista and Launchbaugh, 2001; Mayagoitia González, 2015). Mesquite leaves are available during late spring and early summer before monsoon rains when grasses are typically dormant and low quality. However, mesquite leaves contain secondary compounds, including alkaloids and phenolic compounds (Achakzai et al., 2009; Witmore, 2009), which limit intake by livestock. Animals that can consume small amounts of mesquite may be more adapted to southwestern rangelands than animals that avoid mesquite. Development of a method to cost effectively determine the amount of mesquite in cattle diets would facilitate selection of animals more adapted for rangelands in the southwestern United States.

Near-infrared reflectance spectroscopy (NIRS) has a long history as a spectroscopic technique with useful applications in agriculture (Williams and Norris, 2001) and ecology (Foley et al., 1998). In contrast,

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Table 1
Dry matter (DM), crude protein, neutral detergent fiber (NDF), and acid detergent fiber (ADF) of the honey mesquite leaves, beardless wheat hay, Bermuda grass hay, Sudan grass hay, and timothy hay expressed on a DM basis

Diet item	DM, %	Crude protein, %	NDF, %	ADF, %
Honey mesquite leaves	96.27	16.39	40.10	33.21
Bermudagrass beardless wheat hay	95.93	7.75	62.66	42.53
Sudan grass hay	95.23	5.19	58.86	41.29
Timothy hay	95.31	12.02	57.18	36.46

Raman spectroscopy has not been as widely applied because of early difficulties with sample degradation and fluorescence; however, many of these problems have been overcome (Yang and Ying, 2011) and portable field instruments are now available. NIR spectra originate from absorption of light by vibrating and rotating molecules, and Raman spectra originate from scattering of light by vibrating and rotating molecules. NIRS detects vibrations when the electrical dipole moment changes, while Raman spectroscopy identifies vibrations caused by electrical polarizability changes. NIR spectra are characterized by broad, often overlapping peaks that are matrix dependent and affected by moisture content. In contrast, Raman spectra have narrow, highly resolved peaks that are not affected by matrix or moisture. Another advantage is that mononuclear diatomic molecules (O_2, N_2 etc.) are Raman active but do not absorb in the NIR range. However, an electrically unsymmetrical bond may be NIR active and Raman inactive or both NIR and Raman active (Anderson, 1973; Colthup et al., 1990). Disadvantages of Raman are weak signal-to-noise ratio, sample heating, and sample fluorescence. Because Raman is a weak process, it requires high power and high sample purity. Consequently, Raman is most commonly used for homogenous samples and NIRS is often used for heterogeneous samples. Both methods have advantages and limitations but can be used as complementary methods. For example, studies on bond angles, bond lengths, and other structural information require Raman data in addition to NIR analysis (Yadav, 2005).

Previous studies using diet/fecal pairs and NIRS (f.NIRS) to predict diet composition have used dried and ground feces (Walker et al., 1998, 2002). Because Raman spectroscopy has the potential to be effective without processing of feces and portable instruments are available, the objective of this study was to compare f.NIRS with Raman for predicting the percentage of mesquite in cow feces and the discrimination of base diets by the two techniques.

Methods

Feeding Trial

This research was conducted at New Mexico State University Campus Livestock, Education, and Research Center (Las Cruces, New Mexico) during November and December 2013. Fecal material was obtained from a feeding trial where known amounts of honey mesquite leaves were introduced intraruminally into six ruminally fistulated cows. Cows were mature Hereford × Angus crosses with an average weight of 568 kg. Honey mesquite leaves were harvested from the Chihuahuan Desert Rangeland Research Center located 35 km north of Las Cruces, New Mexico during July 2013. Leaves were harvested by hand and allowed to air dry. During a 14-d pretrial period, animals were fed beardless wheat hay (*Triticum aestivum* L.) ad libitum. Following the pretrial, two animals were randomly assigned to one of three base diets: timothy hay (*Phleum pratense* L.), a C3 perennial; Sudan hay (*Sorghum sudanense* [Piper] Stapf), a C4 annual; or a 50:50 combination of Bermudagrass hay (*Cynodon dactylon* [L.] *Pers.*), a C4 perennial, and beardless wheat hay, a C3 annual (BBW). Base rations (hay) were fed, and refusals were collected and weighed daily. The base hay rations were fed for four periods of increasing levels of mesquite. The initial period was 9 d, in which no mesquite was fed and base diet was fed at 2% of body weight. The subsequent periods were 7 d each. For the second period, the base diet was fed at 1.9% of body weight and 1% of the diet was mesquite leaves. For the third period, the base diet was fed at 1.7% of body weight and 3% of the diet was mesquite leaves. For the fourth period, the base diet was fed at 1.5% of body weight and 5% of the diet was mesquite leaves. Each morning at approximately 0800 hr during the final three periods, air-dried mesquite leaves that were ground to an approximate length of 1 cm were introduced through a rumen cannula. Fecal samples were collected at the same time on the final 2 days of each period. Previous research (Walker et al., 2010) showed that NIR-determined percentage juniper in the diet of goats did not change after the third day when percentage juniper in the goat diet increased from 0% to 10%. Mesquite leaves and the base rations

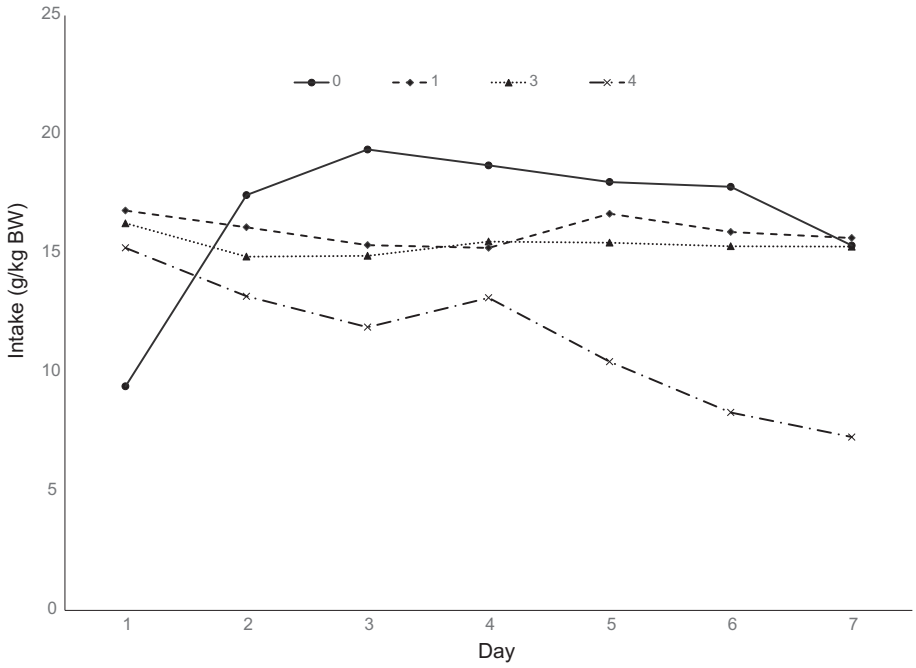

Figure 1. Hay intake (g/kg BW) averaged across three different hays as affected by mesquite as a percentage of total intake placed in the rumen.

Table 2
Calibration, cross validation, and validation statistics for partial least squares regression of near-infrared reflectance spectroscopy and Raman spectra to predict percentage mesquite in cattle diets

	Method	Mean	Stdev	Factors	Slope	Intercept	r^2	RMSE	SEP	Bias	RPD
Calibration	NIRS	2.56	1.80	3.00	0.78	0.55	0.78	0.93	0.95	0.00	2.1
	Raman	2.56	1.23	3.00	0.37	1.61	0.37	1.59	1.61	0.00	1.3
Cross validation	NIRS	2.57	1.77	3.00	0.73	0.71	0.70	1.11	1.12	0.01	1.8
	Raman	2.68	1.13	3.00	0.02	2.62	0.00	2.26	2.29	0.12	0.9
Validation	NIRS	2.06	2.26	5.00	1.03	1.88	0.88	2.09	0.78	1.95	2.6
	Raman	4.99	1.44	3.00	−0.32	5.80	0.21	3.80	3.00	2.43	0.7

RMSE, root mean square error; SEP, standard error of prediction; RPD, ratio of performance to deviation; NIRS, near-infrared reflectance spectroscopy.

were analyzed for DM, ADF, NDF, and crude protein by SDK Laboratories (Hutchison, KS). Dry matter was determined by oven drying for 3 hr at 105°C ADF (NFTA Method 2.1.4). Acid detergent fiber (ADF) and neutral detergent fiber (NDF) analysis was completed using the filter-bag technique (ANKOM filter bag technique; ANKOM Technology Corp, Fairport, NY). Crude protein was determined by Kjeldahl N (AOAC Method 976.06) multiplied by 6.25.

Spectra Acquisition

All fecal samples were dried at 60°C and ground in a Wiley mill to pass a 1-mm screen and then ground a second time in a Wiley mill to pass a 0.5-mm screen. For f.NIRS analysis, daily fecal samples for each animal were packed into sample cells with a near-infrared transparent quartz cover glass and scanned 32 times using a NIR Systems, Inc. (Silver Spring, MD) model 6500, scanning reflectance monochromator. Reflected energy (log 1/R) was measured, averaged over the 32 scans and recorded at 2-nm intervals from 400 to 2 500 nm (wavenumbers 4 000–25 000 cm^{-1}). A personal computer, interfaced to the monochromator, used ISI NIRS2 version 3 software (Infrasoft International, Port Matilda, PA) to collect spectra. Raman spectra of the ground samples were acquired with a Rikagu handheld Raman analyzer with 1 064 nm continuous wave laser. The spectra were collected in the wavenumber range of 200 − 2000 cm^{-1}. Feces were placed in a sample vial supplied with the instrument, and each sample was scanned eight times by rotating the vial 45 degrees between each scan. Each scan consisted of the average of 5 spectra collected during a 2-second acquisition time. Data from the eight scans were averaged for analysis.

Data Analysis

Daily hay intake (g/kg BW) was analyzed for the fixed effect of hay with percentage mesquite and day as repeated measures using PROC GLM (SAS, 2004).

The Unscrambler 9.7 (Camo SoftwareAS, Oslo, Norway) was used to perform pretreatment and partial least squares (PLS) regression (Haaland and Thomas, 1988). For the f.NIRS analysis, the number of spectra was reduced by averaging three adjacent wavelengths, smoothed with a three-segment moving average, and finally a second derivative was calculated with the Savitzky-Golay method (Savitzky and Golay, 1964) using a second-order polynomial and a five-segment gap. The transformed data were mean centered and, to avoid overfitting the number of factors to include in the regression model, PLS regression was conducted with cross validation using a random leave out of 12% of the observations. The Raman spectra were transformed by applying a baseline correction using detrend with a third-order polynomial, standard normal deviate, and a Savitzky-Golay first-order polynomial 31 point smooth. The transformed data were not mean centered, and partial least squares regression was conducted with cross validation described previously. Validation was performed for f.NIRS and Raman spectra using spectra from the Sudan- and timothy-based diets for calibration and predicting the Bermuda beardless wheat hay diets for validation.

Discriminant analysis (SAS, 2004) was used to determine if the untransformed spectra could be used to classify the three hays used in the base diets. To avoid singular matrices that were caused by high multicollinearity of the spectra, stepwise discriminant analysis (PROC STEPDISC) with probability of entry and staying set at $P \leq 0.05$ was used to select the wavenumbers for canonical discriminant analysis. Data were divided into calibration and test sets, and canonical discriminant analysis (PROC DISCRIM) was used to determine if the hays could be correctly classified. Four test set classifications were performed using a leave-out one level of mesquite whereby all samples at three levels of mesquite were used for development of the discriminant function to classify the samples in the left-out levels. Thus, four test and calibration sets were evaluated.

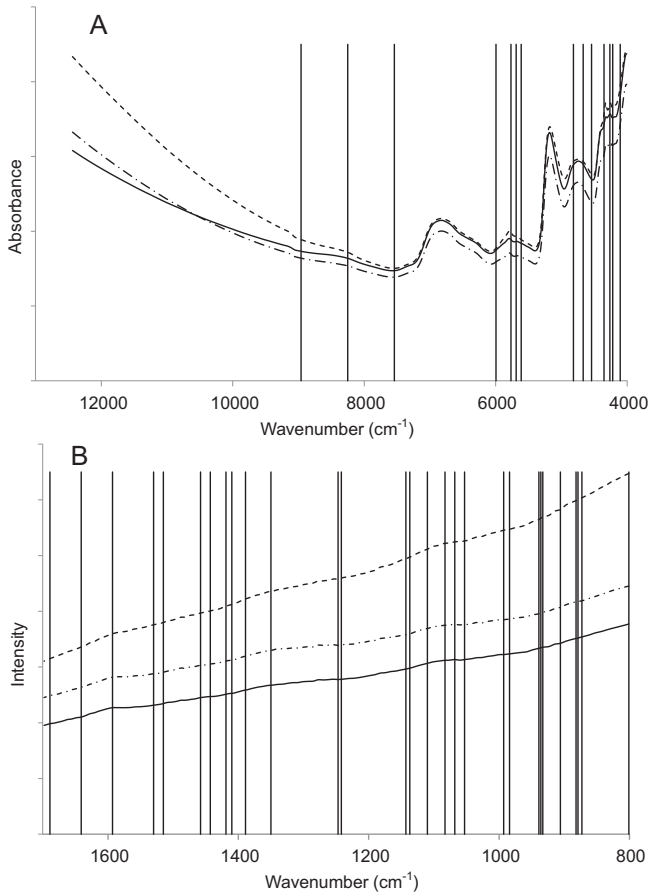

Figure 2. Average near-infrared reflectance spectroscopy (**A**) and Raman (**B**) spectra from feces of animals fed BW, Sudan, and timothy hays with no mesquite. Vertical lines show the location of wave numbers selected for canonical discriminant analysis.

Results

Honey mesquite leaves had a higher crude protein concentration than the hays (Table 1). Mesquite leaves also contained less neutral detergent fiber (NDF) and acid detergent fiber (ADF). The dry matter content of the mesquite leaves was slightly higher than the hay rations. Timothy was the highest-quality hay followed by BBW. Sudan was the lowest-quality hay, and the CP level of this hay was below the maintenance requirement of beef cattle (NRC, 2000) and the requirement of ruminant bacteria (Van Soest, 1982). Intake did not differ between hays ($P > 0.47$), day ($P > 0.11$), or their interaction ($P > 0.78$). There was an effect of percentage mesquite ($P < 0.01$) and the mesquite by day interaction ($P < 0.02$) Figure 1.

Calibration, cross validation, and validation results for predicting percentage mesquite in the diets are shown in Table 2. f.NIRS spectra provided useful calibrations, but Raman spectra did not. f.NIRS cross validation indicated the optimal number of factors in the model was three. However, validation results showed that a five-factor model gave the best results. Precision improved for validation compared with cross validation ($r^2 = 0.88$ and 0.70, respectively). Increasing factors in the cross validation model to more than three decreased the simple coefficient of determination (r^2). The slope of the validation data (1.03) was also improved compared with the cross validation data (0.73). Statistics that measure accuracy, root mean square error and bias, were greater for the validation data (2.09 and 1.95, respectively) than for the cross validation data (1.11 and 0.01, respectively). The ratios of performance to deviation (RPD) were 1.8 and 2.6 for cross validation and validation, respectively.

Raman and f.NIRS spectra on which the stepwise discriminant analysis was performed are shown in Figure 2. Fifteen of 350 possible wavenumbers for f.NIRS spectra and 29 of 300 possible wavenumbers for Raman spectra met the $P \leq 0.05$ entry and staying criteria for the stepwise discriminant procedure (Table 3). Canonical discriminant analysis of the wavenumbers selected in the stepwise procedure showed that Raman and f.NIRS spectra could classify all observations with 100% accuracy and that separation of diets was greater for Raman spectra compared with f.NIRS spectra (Fig. 3). All test data sets were also classified with 100% accuracy (data not shown). Coefficients of the canonical discriminant functions of Raman spectra showed that lignin and hemicellulose were the most important variables for both the first and second discriminant functions (see Table 3). The first canonical discriminant function equally separated BBW, Sudan, and timothy, and the second discriminant function further separated Sudan from BBW and timothy (Fig. 3B). Coefficients of the canonical discriminant function of f.NIRS spectra showed that starch, protein, and oil were the most important variables for the first discriminant function (75%

Table 3
Standardized canonical coefficients of discriminant functions based on Raman and near-infrared reflectance spectroscopy spectra of cattle feces for discriminating between base hay diets. Spectra are listed in order of importance of the coefficient (i.e., absolute value) to the discriminant function. Compounds are the compounds associated with the wavenumber

Raman				Near infrared			
Wavenumber (cm^{-1})	Coeff1	Coeff2	Compound	Wavenumber (cm^{-1})	Coeff1	Coeff2	Compound
936	−9770	−17390	Lignin[1]	2370	404	137	Starch[9]
933	5265	8095	Lignin[1]	2346	−386	−173	Protein[10]
939	3350	8458	Lignin[1]	1212	−270	55	Lipid[9]
1242	1444	773	Hemicellulose [1]	2316	186	−146	Starch[9]
1257	1342	−627	Pectins[2]	1326	159	13	Lignin[11]
1068	1335	−724		2436	−143	−62	
882	−996	−2115	Hemicellulose[3]	1116	127	−58	Water[9]
906	996	151	Cellulose[4]	1668	−121	−23	Protein[3]
1443	970	392	Lipids/fatty acids[3]	1782	100	156	Cellulose[10,12]
1530	−931	−117	Carotenoids[3]	1734	−98	175	Hemicellulose[13]
993	891	204	Cellulose[4]	1758	86	−388	Lipid[9]
1419	737	1244		2142	72	−246	Lipid[10]
984	−645	−489	Xylan[1]	2202	−63	123	Lignin[10]
801	604	393	Lignin[5]	2076	−19	174	Cellulose[12]
1458	543	−943	Cellulose[10]	2298	−18	268	Cellulose[10]
873	523	1094	Hemicellulose[6]				
1593	−426	−601					
1410	402	−314	Cellulose[4]				
1110	383	122	Noncellulosic structural polysaccharides[7]				
1137	−362	4	Lignin[1]				
879	301	904					
1389	−280	−382	Lignin[1]				
1515	−241	300	Lignin[1]				
1053	228	591	Cellulose[4]				
1083	−227	623	Starch[6]				
1350	194	311					
1143	−165	−272	Cellulose[8]				
1641	40	474	α-pinene[3]				
1689	33	−152					

[1] Agarwal, 1999
[2] Copikova et al., 2003
[3] Schultz and Baranska, 2007
[4] Wiley and Atalla, 1987
[5] Larsen and Barsberg, 2010
[6] Holder, 2012
[7] Kacurikova et al., 1998
[8] Schenzel and Fisher, 2001
[9] Williams and Norris, 2001
[10] Workman and Weyer, 2007
[11] Sun et al., 2013
[12] Sieler et al., 2002
[13] Chen et al., 1997

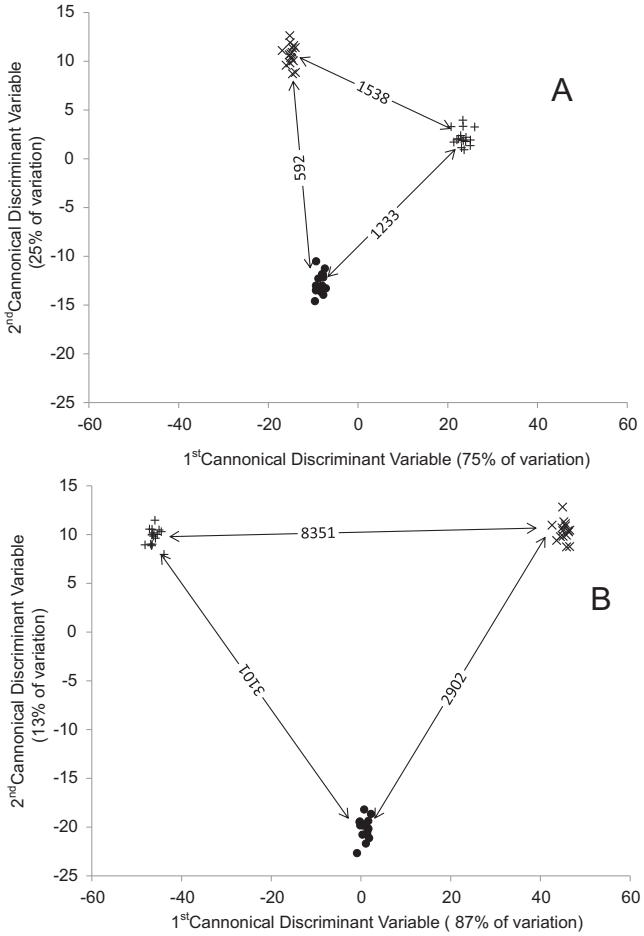

Figure 3. Plot of canonical discriminant scores from discriminant analysis of fecal near-infrared reflectance spectroscopy (**A**) and Raman (**B**) spectra to discriminate among hay diets: x BW; ● Sudan; + Timothy. Axes show percent of variation in spectra accounted for by each Eigen vector. Double-headed lines show the squared Mahalanobis distance between the center of each group.

of variation), which primarily separated BBW and Sudan from timothy. The most important canonical coefficients on the second function (25% of variation) for f.NIRS spectra were associated with lipid and cellulose and separated BBW from Sudan on this axis. (See Fig. 3A).

Linear discriminant functions for Raman spectra indicated that classification of BBW and Sudan diets was based on lignin peaks but at different wavenumbers. Classification of timothy was also based on lignin, but hemicellulose and carotenoids were also important. Linear discriminant functions for f.NIR spectra showed that classification of BBW and Sudan diets was based on protein and lipid peaks but at different wavenumbers. Classification of timothy was based on lignin, starch, and water peaks.

Discussion

The improvement in validation statistics for the f.NIRS spectra obtained by adding two additional factors was presumably because the additional factors accounted for matrix effects caused by different base diets on the spectra. This suggests that when predicting independent samples whose base diets differ from the calibration diets, the usual case for fecal diet calibrations, increasing the number of factors above the optimal number indicated by cross validation may be useful. This may be particularly applicable when the number of factors in the calibration model is small, as was the case in this study. The ratio of performance-to-deviation (RPD) values for cross validation (1.8) and validation (2.6) indicate that the former would be useful for distinguishing between high and low values, and the latter for approximate quantitative predictions (Saeys et al., 2005). These results indicate that f.NIRS is a viable method for estimating consumption of mesquite in the diets of cattle and are considered quite good because previous studies (Walker et al., 2010) that used f.NIRS of diet fecal pairs had much wider ranges in the percentage of the plant species in the diet used for calibration. In that study, four different species were investigated and the range of percentages of the species in the diets was a minimum of 24 percentage units and a maximum of 100 percentage units, while this study had a range of only 5 percentage units for mesquite. Cross validations r^2 were all above 0.90, and RMSE ranged from 1.9–5.6 percentage units for the species in Walker et al. (2010) compared with $r^2 = 0.70$ and RMSE = 1.11 percentage units for this study. Raman spectra did not predict percentage mesquite in the diets because there was no pattern in intensity of spectra at different levels of mesquite, either within a hay or between hays. The cause of this is not clear.

In contrast to the poor performance of Raman relative to f.NIRS for predicting percentage mesquite in the diet, Raman spectra were better able to discriminate among the base hay diets. The better discrimination by Raman was because there were large differences in intensity for feces from the three hays (see Fig. 1B), while f.NIRS spectra often overlapped and crossed. Feeding mesquite at the 5% level resulted in diarrhea and a reduction of intake for some animals after the second day at this level. Baptista and Launchbaugh (2001) also reported decreased intakes in diets above 5% mesquite. This indicates that low levels of mesquite could affect rumen function and animal physiology, resulting in a reduction of intake. The metabolic effects of consuming mesquite could cause matrix differences in feces that were detected by f.NIRS but not Raman. Near-infrared spectroscopy is sensitive to physical differences in scanned materials (Williams and Norris, 2001) while Raman spectroscopy is not, which may explain why useful calibrations for percentage of mesquite in the diet could be developed for f.NIRS spectra but not Raman spectra.

Differences in the canonical discriminant analysis of Raman and f.NIRS spectra provide insight into the differences between these two spectroscopic techniques. Discrimination using Raman spectra was primarily associated with wavenumbers associated with undigestible constituents of the diet (i.e., lignin). In contrast, discrimination using f.NIRS spectra was primarily associated with wavenumbers associated with digestible constituents in the diet (i.e., protein, starch, and lipid). Raman spectroscopy is most commonly used to identify specific chemical compounds based on well-defined spectral bands; however, in this study, similar to f.NIR, the discrimination of hay diets by Raman spectra was the result of differences of spectral intensity between feces from animals consuming different hays.

Implications

This study showed that f.NIRS has the potential to, at a minimum, predict high and low consumers of chemically defended plants such as mesquite that are only consumed in small amounts. This information can be used to help select animals that have a higher intake of these plants and thus have a greater potential to more effectively utilize the vegetation in areas where species such as mesquite are abundant.

This is the first study to demonstrate that Raman spectroscopy has the potential for discriminating among animals that are consuming different diets. Because in contrast to NIR, water does not affect Raman, and because field-friendly, hand-held Raman spectrometers, such as the one used in this study, are readily available, this technology has a great potential for ecological field studies. NIRS spectroscopy has shown great potential in ecological studies (Foley et al., 1998; Vance et al., 2016). We believe that Raman spectroscopy deserves further investigation as a quantitative technique in ecological field studies.

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