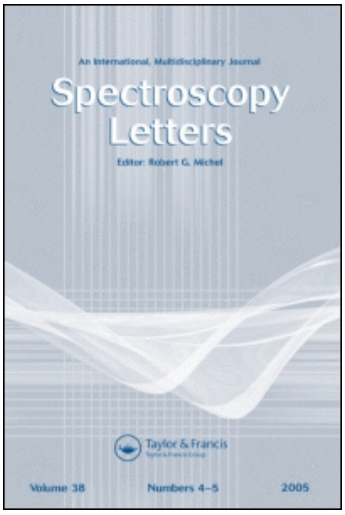


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# EFFECTS OF APODIZATION FUNCTION, ZERO FILLING, BACKGROUND SPECTRA, AND ABSORBANCE TRANSFORMATION ON MID-INFRARED CALIBRATIONS FOR FEED COMPOSITION

James B. Reeves III[a]; Valerie B. Reeves[b]
[a] AMBL, ANRI, ARS, USDA, Beltsville, MD, U.S.A. [b] CVM, Rockville, MD, U.S.A.

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# EFFECTS OF APODIZATION FUNCTION, ZERO FILLING, BACKGROUND SPECTRA, AND ABSORBANCE TRANSFORMATION ON MID-INFRARED CALIBRATIONS FOR FEED COMPOSITION

**James B. Reeves III[1,*] and Valerie B. Reeves[2]**

[1]AMBL, ANRI, ARS, USDA, Bldg 306, Rm 101, BARC East, Beltsville, MD 20705
[2]CVM, FDA, 7500 Standish Place, Rockville, MD 20855



## ABSTRACT

Research has demonstrated that diffuse reflectance mid-infrared spectroscopy can, like near-infrared diffuse reflectance, be used to quantitatively determine the composition of ground samples of forages and soils without the need for KBr dilution. While it has been demonstrated that the accuracy of calibrations developed using mid-infrared spectra can be equal to or better than that achieved using near-infrared

*Corresponding author. E-mail: jreeves@anri.barc.usda.gov



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spectra, the influence of factors such as apodization function has not been determined. Results based on the spectra of 173 treated forage samples obtained using a DigiLab FTS-60 spectrometer have demonstrated that many parameters associated with mid-infrared spectra have little or no effect on partial least squares calibrations. Additional zero filling of spectra had little effect other than to increase the derivative gaps found to produce optimal calibrations, but calibrations developed using Kubelka-Munk transformed data, as opposed to absorbance data, were not as accurate. Choice of apodization function also had little effect, although slightly better results were found using triangular or weak Norton-Beer. Likewise, the frequency of taking a background spectrum did not seem to have any great effect on calibrations, although results were slightly better with hourly or daily acquisitions as opposed to one for each sample as is done in the near-infrared.

*Key Words*: Apodization function; Zero filling; Background spectra; Absorbance transformation; Mid-infrared calibrations; Feed composition; Multivariate analysis



## INTRODUCTION

While diffuse reflectance spectroscopy has, over the last couple of decades, come to be used extensively in the near-infrared (NIR) spectral range for the quantitative analysis of products ranging from agricultural products[1] to pharmaceuticals[2] and gasoline[3] with literally thousands of references, the use of mid-infrared diffuse reflectance Fourier transform spectroscopy (DRIFTS) for the same analysis has been much more limited and more recent. This has, at least in part, been due to the belief that samples needed to be diluted with KBr to concentrations of less than 10% in order to obtain usable spectra. Dilution being needed due to artifacts produced at the high levels of absorbance resulting when non-diluted samples are examined.[4–6]

However, recent work with a variety of food products,[7–10] forages,[11–12] and soil samples[13,14] has demonstrated that DRIFTS on non-KBr diluted samples can be used with an accuracy equal to or better than that achieved using NIR spectra. While most of the NIR work has been carried out using instruments with parameters such as resolution predetermined (i.e., fixed resolution and bandwidth scanning monochromators

and even filter based instruments), this is not the case with Fourier transform mid-infrared spectrometers (FTIR) where many, if not most, functions including resolution, apodization function, or degree of zero filling may be chosen by the user. Also, many if not most, NIR instruments in use have an automated procedure for obtaining a background spectrum. For example, the NIRSystems model 6500 (FOSS NIRSystems, Silverspring, MD) and earlier 6000 series instruments use a ceramic standard which is automatically read either before and/or after the sample is scanned. With an FTIR, the user must prepare a suitable standard and determine how often to obtain a new background. In earlier work, we did this only once a day with excellent results.[10–12,14] In those studies, the default settings for the instrument were used for apodization (triangular), zero filling (none), and spectral form (diffuse absorbance), although some studies of the effect of resolution and number of co-added scans taken were carried out.[11] While, as stated, studies have shown that results using mid-infrared (mid-IR) spectra can be as good or better than those obtained using NIR spectra, the question of whether results can be improved by using different parameter settings has not been answered.

Examination of the literature reveals a variety of opinions on exactly what apodization function, etc., provides the best spectra for quantitative analysis. Compton and Compton[15] state that generally triangular, Norton-Beer, or Happ-Genzel are used for spectra of non-gas phase spectra. Smith[16] states that for quantitative analysis the medium Norton-Beer function gives the best results, but that it is up to the user to determine which function is best for a given application. Griffiths and de Haseth[17] state that the most common function used is triangular apodization (instrument default), but that for good quantitative accuracy, the weak Norton-Beer function is recommended.

Zero filling a spectrum results primarily in changes in band shape, and while recommended by many texts, no discussion on its effect on quantitative analysis was found.[15,18] The Kubelka-Munk function is designed to relate peak height or areas to concentration for quantitative analysis, and according to Smith[16] "must" be used for quantitative analysis with DRIFTS, although it has not been found to be useful for NIR spectra obtained by diffuse reflectance. Workman and Springsten[19] similarly state that its application to non-diluted samples obtained by DRIFTS can help to linearize the data for quantitative analysis.

One final consideration to the above discussion needs to be considered with respect to the chemometric method by which most quantitative analysis in the mid-IR has been carried out. Much, if not most, quantitative analysis based on mid-IR spectra has been performed using mixtures of known substances with quantitation determined by the solution of simultaneous

equations.[20] At the present time, much, if not most, of the quantitative analysis performed using NIR spectra is based on partial least squares (PLS) regression with spectra often pre-treated in a variety of ways including mean and variance scaling, multiplicative scatter correction, and 1st and 2nd derivatives. Thus, the spectra used are often not the same as those used in earlier work from which conclusions on apodization, zero filling, etc., were drawn. The objective of this work was to examine the effects of instrument variations, as reflected by the frequency of obtaining background spectra, and instrument functions, such as type of apodization, on mid-IR calibrations for feed composition using PLS.

## MATERIALS AND METHODS

### Samples

One hundred and seventy three samples from a forage treatment study were evaluated. These samples came from a study designed to increase forage digestibility involving the treatment of sixteen different forages and by-products, including hays (alfalfa, orchardgrass, etc.), corn cobs, stovers (corn and soybean), wheat straw, and hulls (peanut, rice, and soybean), at eleven sodium chlorite concentrations (0.0 to 0.4 g/g of forage). In the original study,[21] two samples were lost for a final total of 174. In this study, one sample was improperly scanned and was removed leaving 173 samples. Due to the work on timing of the background spectra, this sample was not rescanned and added to the study.

### Analytes

All samples were analyzed on a dry matter basis for various measures of fiber composition, digestibility, and total Kjeldahl nitrogen (measure of crude protein content), measures commonly used to evaluate the quality of ruminant feedstuffs.[22,23] Further details on the exact procedures can be found in Reeves, 1987.[21]

### Spectra

All spectra were obtained using a Digi-Lab FTS-60 FTIR (Bio-Rad, Cambridge, MA) equipped with a KBr beam splitter, DTGS detector, and diffuse reflectance accessory (Bio-Rad, #925-0044). The optical path of the

diffuse reflectance accessory is described in reference 11. All spectra were collected as interferograms at 4 $cm^{-1}$ resolution from 4000 to 400 $cm^{-1}$ with 64 co-added spectra collected per spectrum. Samples were scanned "as is" or "neat" with no KBr dilution using a custom made sample cell transport which allowed a sample area approximately $2 \times 50$ mm long to be scanned. This custom made cell replaced the four single cells supplied with the diffuse reflectance accessory.[11] Each sample was scanned once and only once and collected as an interferogram to eliminate the influence of different subsamples being used for different spectral computations (various apodizations, etc.). Samples were ground to pass a 20 mesh screen using an UDY cyclone grinder. Potassium bromide was used for the background spectra. A background spectrum was taken immediately before each sample was scanned and also stored as an interferogram. One background sample was packed in a cell and used through out the day. Samples were randomized before scanning in order not to induce order into the data set.



## Spectral Parameters Examined

### Zero Filling and Absorbance vs. Kubelka-Munk Transformation

Spectra as obtained on the Digi-Lab system had one data point every 1.92 $cm^{-1}$ when collected at 4 $cm^{-1}$ resolution for a total of 1861 data points per spectrum. Additional zero filling of 1 and 2x were studied resulting in 3733 and 7466 data points per spectrum, respectively. Background spectra were similarly zero filled and used to create appropriate diffuse absorbance spectra. For this part of the study, the background spectrum taken with each sample was used for the particular sample in question with triangular apodization (instrument default). The same sample and background interferograms were used for each sample for all transformation comparisons. Spectra created using no additional zero filling (1861 data points), 4 $cm^{-1}$ resolution, triangular apodization, and background spectra collected immediately before each sample spectrum were used to examine the effect of absorbance versus Kubelka-Munk transformation of the single beam spectra.

### Apodization Function

Eight apodization functions were examined: Boxcar, Cosine, Happ-Genzel, Bessel, weak Norton-Beer, medium Norton-Beer, strong Norton-Beer, and Triangular. Again, 4 $cm^{-1}$ resolution spectra with no

additional zero filling and background spectra collected immediately before each sample spectrum were used. As before, the same sample and background interferograms were used for each sample for all transformation comparisons.

### Frequency of Background Spectra

Single beam spectra were transformed using backgrounds obtained individually for each spectrum, obtained at the beginning of an hour of scanning (Hourly), and using the first background spectrum obtained each day (Daily). The default settings of triangular apodization and 1861 data points per spectrum ($4\,cm^{-1}$) resolution were used, with spectra computed in the diffuse absorbance mode. While the background interferogram changed, the same sample interferogram was used for each transformation examined.



## PLS and Statistics

All results reported are from one-out cross validations obtained using Galactic's PLSPlus version 2.1 G and PLS1 (Each analyte regressed independently) running under GRAMS/32 version 3.2 (Galactic Industries, Salem, NH). All spectra were mean centered and variance scaled with a variety of 1st and 2nd derivatives examined with all data from 4000 to $500\,cm^{-1}$ used. Multiplicative scatter correction was also tested but was not found to be of any additional help. The number of factors chosen was selected using the F-test from the one-out cross validation PRESS statistic. All samples were used in all calibrations with no samples removed as outliers. The results reported are for the relative mean squared deviation (RMSD) statistic. Each calibration was optimized for the specific spectral configuration examined.

# RESULTS AND DISCUSSION

## Analytes

Table 1 presents the range of values for the various analytes examined. Due to the chlorite treatment, the range in values for many of the analytes was quite large, especially for the two measures of digestibility, cell wall (CWDG) and total dry matter (DMDG). The values above 100% for these analytes were due to slight errors in corrections for ash content.

***Table 1.*** Sample (n = 173) Composition on a Dry Matter Basis

| Variable[1] | Mean | Std. Dev. | Minimum | Maximum |
|---|---|---|---|---|
| NDF | 68.36 | 14.31 | 33.43 | 91.58 |
| ADF | 47.35 | 10.59 | 26.61 | 80.32 |
| Lignin | 9.37 | 5.39 | 2.47 | 26.21 |
| CWDG | 65.69 | 27.19 | 1.52 | 100.23 |
| DMDG | 74.91 | 22.01 | 11.47 | 100.15 |
| CP | 7.87 | 5.22 | 1.55 | 16.84 |

[1]NDF = Neutral detergent fiber, ADF = acid detergent fiber, CWDG = cell wall digestibility, DMDG = dry matter digestibility, CP = crude protein.



Treatment with sodium chlorite increases the soluble ash content of the samples, and if not accounted for, can make the samples appear more digestible or lower in fiber content than is actually the case.[21] The wide range in values is also due to the variety of forages and by-products treated which ranged from high quality hays to low quality, nearly indigestible, high fiber materials such as peanut hulls. Overall, the data set represented a wide assortment of diverse materials both compositionally and agronomically and thus represent an excellent set for testing the effects of various parameters on PLS calibration accuracy.

## Effect of Zero Filling and Absorbance vs. Kubelka-Munk

Figure 1 demonstrates the effects of zero filling on mid-IR spectra. As shown, the primary effect is to make peaks smoother by essentially interpolating between existing data points resulting in slight changes in the exact peak position and shape. These changes are more likely to be of importance in spectral interpretation or comparison than in quantitative analysis where data smoothing is already often used. In Table 2, the results obtained using various levels of additional zero filling are shown. All of the results shown were quite good with one-out cross validation $r^2$ (no additional zero filling) of: NDF, 0.971; ADF, 0.970; lignin, 0.938; CWDG, 0.954; DMDG, 0.967; and CP, 0.986. The most prominent effect seen was a shift in the derivative found to give the best results to derivatives with higher gaps. Derivatives 1–5 were 1st derivatives with gaps of 4, 8, 16, 32, and 64 data points, while derivative 6–10 were 2nd derivatives with similar gaps. As can be seen, as the number of data points doubled, the derivative gap increased in the same fashion, indicating the need to ratio the same spectral peaks. For three of the analytes (lignin, CWDG, and CP), the lowest errors were found using no

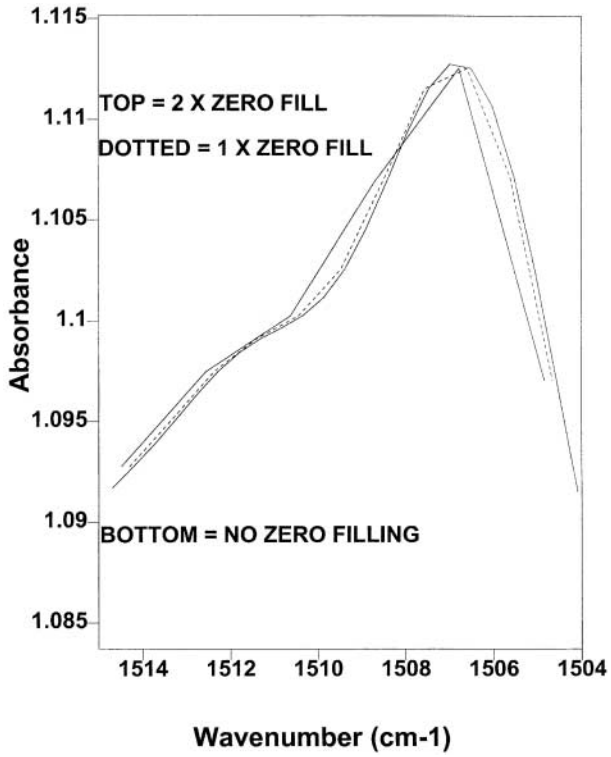


*Figure 1.* Mid-infrared spectrum of forage sample #1 from 1515 to 1504 $cm^{-1}$ demonstrating the effects of zero filling, 1 X shifted by +0.00125 A, 2 X by 0.0025 A.

additional zero filling, while for the others, additional zero filling helped slightly. If one excludes the results for DMDG, the average results were virtually identical for all three levels of zero filling. Overall, these results indicate that additional zero filling does not offer any significant benefits to the development of PLS based calibrations, especially when considered in light of the doubling of the time necessary to develop calibrations with each increase in zero filling.

Although the Kubelka-Munk transformation is said to improve quantitative analytical results for DRIFTS based calibrations, this was not the case here. None of the results found were equal to or better than those found for the diffuse absorbance spectra. On average the RMSD were about 10% higher for the Kubelka-Munk transformed spectra, with the worst results seen for CP (RMSD increased by 25%) and the best for CWDG (RMSD increased by only about 6%). While there are too few analytes here

***Table 2.*** Effect of Degree of Zero Filling on One-Out Calibration Results and Kubelka-Munk vs. Absorbance Transformation on One-Out Cross Validation Results

| | Absorbance Spectra | | | | | | | | | Kubelka-Munk | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No Zero Filling | | | One X Zero Filling | | | Two X Zero Filling | | | No Zero Filling | | |
| Assay[1] | Der[2] | Fact[3] | RMSD[4] | Der | Fact | RMSD | Der | Fact | RMSD | Der | Fact | RMSD |
| NDF | 8 | 12 | 2.444 | 9 | 12 | 2.440 | 10 | 12 | 2.440 | 2 | 14 | 2.896 |
| ADF | 8 | 12 | 1.845 | 9 | 12 | 1.841 | 10 | 12 | 1.836 | 7 | 13 | 2.083 |
| Lignin | 8 | 13 | 1.337 | 9 | 13 | 1.339 | 10 | 13 | 1.342 | 7 | 12 | 1.437 |
| CWDG | 8 | 13 | 5.854 | 2 | 14 | 5.859 | 10 | 13 | 5.866 | 7 | 10 | 6.242 |
| DMDG | 2 | 14 | 4.021 | 2 | 14 | 3.931 | 3 | 14 | 3.930 | 7 | 11 | 4.417 |
| CP | 7 | 13 | 0.610 | 8 | 13 | 0.611 | 9 | 13 | 0.613 | 2 | 14 | 0.767 |
| Average | | | 2.685 | | | 2.670 | | | 2.671 | | | 2.974 |

[1]NDF = Neutral detergent fiber, ADF = acid detergent fiber, CWDG = cell wall digestibility, DMDG = dry matter digestibility, CP = crude protein.
[2]Derivatives 1 to 5 are 1st derivatives with gaps of 4, 8, 16, 32, and 64 data points, respectively. Numbers 6 to 10 are 2nd derivatives with gaps of 4, 8, 16, 32, and 64 data points, respectively.
[3]Number of PLS factors used.
[4]Root mean squared deviation error.

to make any further conclusions, it is also interesting to note that the biggest increases in calibration error (RMSD) was seen for CP which, based on $r^2$, produced the best calibration, and the least increase was seen for CWDG and lignin (7% increase) which produced the poorest calibrations based on $r^2$. Overall, these results offer no support for using the Kubelka-Munk transformation with DRIFTS spectra of neat samples when PLS is used for quantitative analysis. While the Kubelka-Munk transformation may not be of any benefit for quantitative analysis performed using PLS, as shown in Figs. 2 and 3, it results in large changes in the spectra which would need to be considered in spectral comparisons, etc. As shown in Fig. 2, the transformation results in a stretching of the spectrum in the y axis. Fig. 3 (diffuse absorbance spectrum scaled) shows that this effect is also not uniform across the spectral range and also alters the peak shapes.



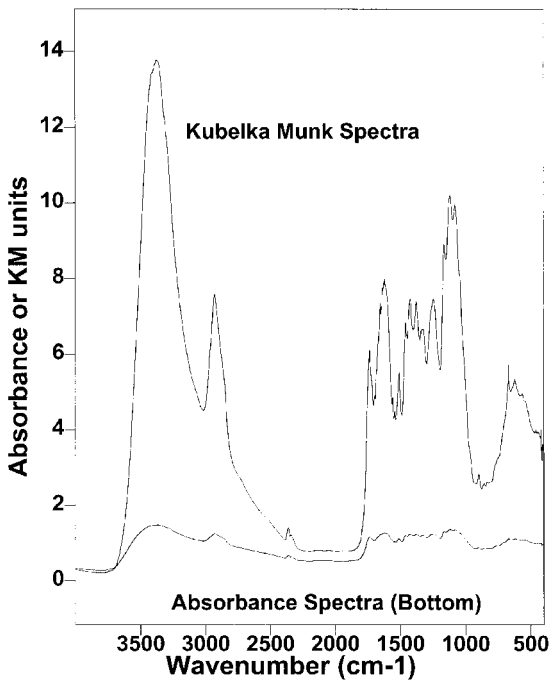


*Figure 2.* Mid-infrared spectrum of forage sample #1 as computed in absorbance and Kubelka-Munk units.

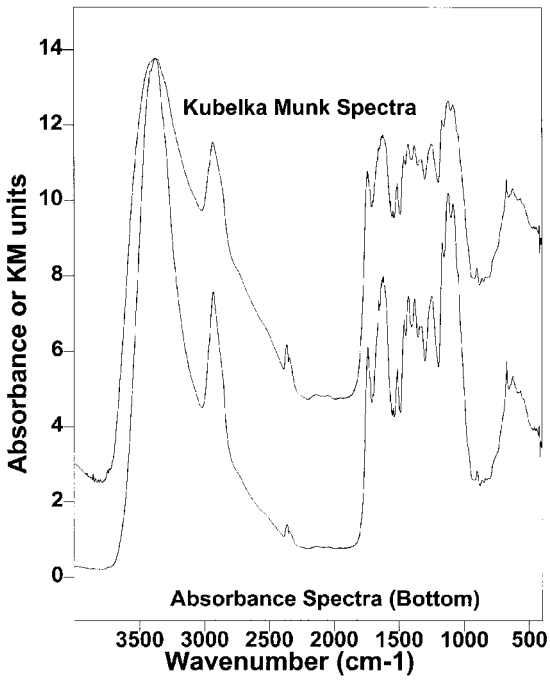


*Figure 3.* Mid-infrared spectrum of forage sample #1 as computed in absorbance units (scaled by factor of approximately 1.5) and in Kubelka-Munk units.



## Apodization Function

The effects of using different apodization functions is shown in Figs. 4 and 5 and Table 3. As demonstrated in Fig. 4, the use of different functions can result not only in shifts in the peak position, but also in the maximum absorbance of the peak. Also notice the slight difference in deflection of the peak at about 1509–1508 for the weak Norton-Beer transformed data as compared to the others. While this effect is slight, it could easily alter the results obtained when spectra are derivatized.

The data in Table 3 shows that overall any of the functions could be used, with the best results seen for the triangular or weak Norton-Beer transforms and the worst for the Boxcar. However, even at the extremes, the increase in average error was only 0.8%. Excluding the Boxcar data, the average RMSD ranged from 2.685 to 2.691 or by approximately 0.22%. Thus, while the apodization function used might well effect spectral peak

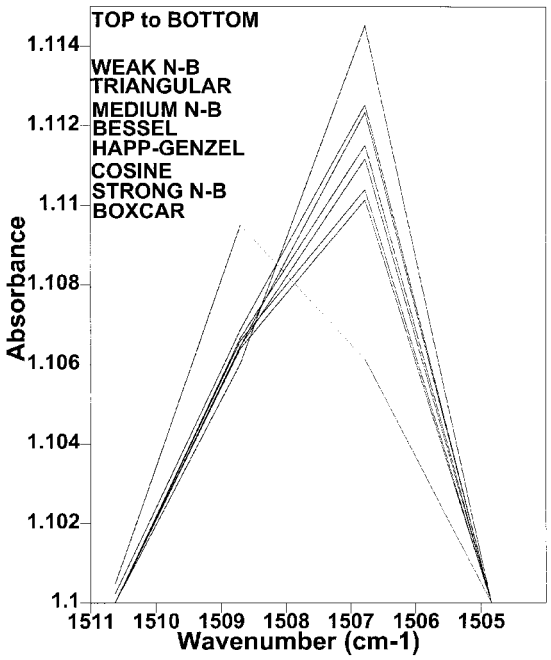


*Figure 4.* Mid-infrared spectrum of forage sample #1 from 1510 to 1505 $cm^{-1}$ demonstrating effects of different apodization functions.



positions or the ability to perform spectral interpretation, it apparently has little, if any, effect on quantitative analysis when using PLS and derivatized spectra. However, as the data in Fig. 4 shows, one could easily see how quantitative analysis based on peak height or area might be influenced by the choice of apodization function.

## Background Spectra

The data in Table 4 show how the frequency of taking a new background spectrum affected calibration accuracy. As with the choice of apodization function, the frequency with which a new background spectrum was taken had remarkably little effect on the final calibration results. Interestingly, taking a background spectrum with each sample gave the poorest results, while hourly and daily acquisition performed about the same. As shown in Figs. 5–7, the background spectrum can vary as much

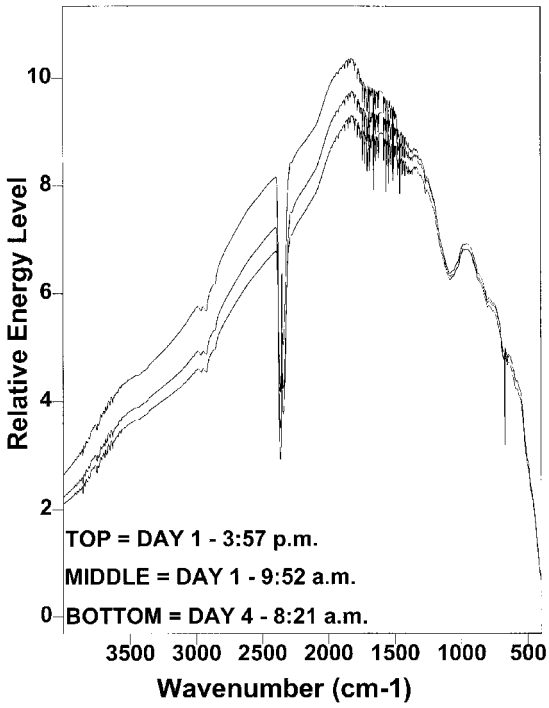


*Figure 5.* Single beam mid-infrared KBr background spectra demonstrating within day and day to day variations.



within a day as from day to day. Since the same sample was used during a single day, most of the variation within a day should be due to instrument changes over time, as demonstrated by the differences in the peaks due to $CO_2$ in the 2300 to 2400 $cm^{-1}$ region or instrument alignment. The fact that day to day variations were often no greater than within a day indicates that differences due to sample packing were minor at best. However, it is possible that the sample may have been disturbed during placement and that this might account for some of the bigger differences seen. In the NIR, a single, constant, ceramic standard is used which eliminates changes due to the sample itself. Perhaps the use of a similar standard would help improve results in the mid-IR. However, at present, the data support the concept that background samples need not be taken more than a few times a day at most, since even with only one per day the results achieved in the mid-IR have been found to be equal to or better than those achieved in the NIR using optimal NIR conditions.[10–12,14]

***Table 3.*** Effect of Apodization Function on One-Out Calibration Error (RMSD) Using Diffuse Absorbance Spectra and One New Background Spectrum for Each Sample (1867 Data Points per Spectrum)

| | Apodization Function Applied[1] | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Assay[2] | BES | BOX | COS | HAP | M-NB | S-NB | TRI | W-NB |
| NDF | 2.448 | 2.544 | 2.443 | 2.444 | 2.447 | 2.441 | 2.444 | 2.446 |
| ADF | 1.852 | 1.828 | 1.810 | 1.851 | 1.849 | 1.808 | 1.845 | 1.847 |
| Lignin | 1.336 | 1.352 | 1.335 | 1.337 | 1.339 | 1.336 | 1.337 | 1.347 |
| CWDG | 5.875 | 5.811 | 5.893 | 5.876 | 5.855 | 5.892 | 5.854 | 5.804 |
| DMDG | 4.023 | 4.058 | 4.027 | 4.026 | 4.024 | 4.029 | 4.021 | 4.026 |
| CP | 0.614 | 0.642 | 0.613 | 0.612 | 0.613 | 0.612 | 0.610 | 0.640 |
| Average | 2.691 | 2.706 | 2.687 | 2.691 | 2.688 | 2.686 | 2.685 | 2.685 |

[1]BES = Bessel, BOX = boxcar, COS = cosine, HAP = Happ-Genzel, M-NB = medium Norton-Beer, S-NB = strong Norton-Beer, TRI = triangular, and W-NB = weak Norton-Beer.
[2]NDF = Neutral detergent fiber, ADF = acid detergent fiber, CWDG = cell wall digestibility, DMDG = dry matter digestibility, CP = crude protein.



***Table 4.*** Effect of Frequency of Background Spectra on One-Out Cross Calibration Errors (RMSD)[1]

| | Frequency of Background Spectra | | |
|---|---|---|---|
| Assay[2] | 1/Sample | Hourly | Daily |
| NDF | 2.441 | 2.417 | 2.445 |
| ADF | 1.808 | 1.791 | 1.739 |
| Lignin | 1.336 | 1.300 | 1.297 |
| CWDG | 5.892 | 5.761 | 5.868 |
| DMDG | 4.029 | 3.800 | 3.855 |
| CP | 0.612 | 0.615 | 0.591 |
| Average | 2.686 | 2.614 | 2.632 |

[1]Root mean squared deviation.
[2]NDF = Neutral detergent fiber, ADF = acid detergent fiber, CWDG = cell wall digestibility, DMDG = dry matter digestibility, CP = crude protein.

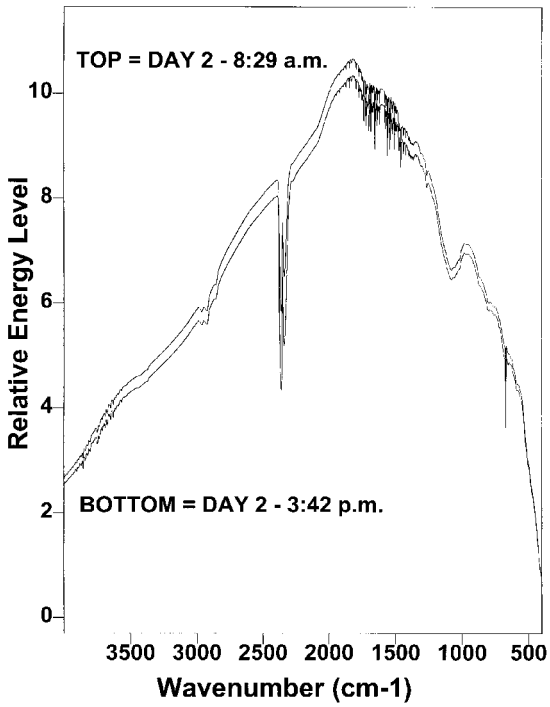


*Figure 6.* Single beam Mid-infrared KBr background spectra demonstrating within day variations.



## CONCLUSIONS

Results using a diverse set of chemically treated forages and by-products have demonstrated that many parameters associated with the computation of mid-IR spectra have little or no effect on calibrations for composition when using PLS. Additional zero filling of spectra had little effect on the final calibrations other than to increase the derivative gaps found to produce optimal calibrations. Calibrations developed using Kubelka-Munk transformed data, as opposed to absorbance data, were not as accurate despite the fact that this transformation was developed for DRIFTS-derived spectra to be used for quantitative analysis. Little effect was seen on the calibrations due to the choice of apodization function, although slightly better results were found using triangular or weak Norton-Beer apodization. Likewise, the frequency of taking a background spectrum did not seem to have any great effect on calibrations, although results were

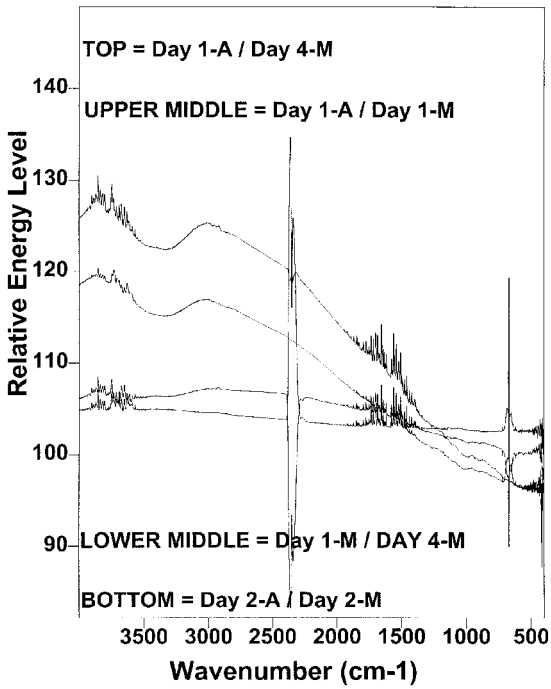


*Figure 7.* Ratios of various background spectra (×100) obtained at the start of the day (M) and at the end of the day (A), see Figs. 5 and 6 for corresponding single beam spectra.



slightly better with the use of hourly or daily acquisitions as opposed to one background spectrum for each sample as is done in the NIR. Finally, while zero filling, type of apodization and frequency of obtaining a background spectrum have little effect on quantitative analysis results, variations in these parameters could easily alter peak shape and position which might be of importance for qualitative analysis or quantitative analysis based on peak height or area.

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