ASSESSMENT OF NEAR INFRARED (NIR) DIFFUSE REFLECTANCE ANALYSIS FOR MEASURING MOISTURE AND WATER ACTIVITY IN RAISINS

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ABSTRACT

Near Infrared (NIR) Analysis was applied to assess its potential for measuring water activity ($a_w$) and moisture in California Seedless Raisins in moisture equilibrium and nonequilibrium conditions. Samples covered a wide range of anticipated moisture contents. An NIR calibration for $a_w$ was made for whole raisins that were fully equilibrated. For ground raisins, NIR calibrations were made both $a_w$ and vacuum oven moisture, covering a large range of moisture contents and equilibrium conditions. Direct measurement of $a_w$ by a dewpoint device gave highly repeatable results, especially for ground raisins. Vacuum oven analysis of moisture was less precise than $a_w$ measurements. Full spectrum NIR calibrations indicated that NIR could predict $a_w$ of raisins in ground form, irrespective of their state of hydration beyond three hours following processing. A much larger sample population will be needed to establish precise calibrations for vacuum oven moisture.

INTRODUCTION

California Seedless Raisins comprise the largest dried fruit commodity produced in the United States, in terms of both quantity and value. Annual production is usually about 350,000 to 400,000 tons with a farm value of about a half billion dollars. Raisins are also a most important export item, as about one third of the total production is shipped to foreign markets.

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Establishing and assuring high quality standards for raisins and raisin products is necessary to maintain and enhance the viability of the industry. Raisins are graded for quality, moisture, mold contamination, and the presence of various foreign materials, as they are delivered to processing plants ("incoming") and again immediately following processing, prior to shipment ("outgoing"). The Agricultural Marketing Service of the United States Department of Agriculture, which develops and implements the various grading procedures (USDA 1989), conducts raisin grading.

In earlier work, Huxsoll et al. (1995) we showed that near infrared (NIR) and analysis had potential for predicting visual quality grade and moisture for incoming raisins. We also showed that NIR could be used to predict water activity (a_w) in whole raisins that were fully equilibrated (Huxsoll).

The a_w of foods and food ingredients has been widely studied and described. The same parameter was originally called the equilibrium relative humidity (ERH), the ratio of the water vapor pressure of a product to the vapor pressure of pure water at the same temperature. Water activity relates to the chemical potential of water in food systems, and is expressed as a fraction, in decimal form, between 0 and 1. For most food systems a_w is a more meaningful parameter than the moisture content, because it describes the chemical and functional state of the water as well as its amount. The water activity of a product is a measure of the energy state of the water in a food system, and may be influenced by several factors. Many models have been proposed to predict a_w for specific food systems (Rahman 1995), but these models are primarily of academic interest. Most food systems are very complex and several factors determine a_w values Labuza 1984).

Moisture and a_w relationships in prunes and raisins were examined by Bolin (1980). He utilized a Warburg apparatus to equilibrate sun-dried raisins and dehydrated grapes with saturated solutions of various salts of known water activities. The moisture contents of equilibrated samples were determined by drying in a vacuum oven. This work showed, as expected, that the maturity quality of the grapes prior to harvest influenced the relationship between water activity and moisture. Raisins made from grapes of higher maturity quality at harvest contained greater amounts of solids, and therefore had lower a_w values at specific moisture contents, than raisins made from lower quality grapes. Bolin developed two second-order polynomial equations to express moisture content as a function a_w. One equation was for raisins made from grapes that were harvested at 22° Brix and the other for raisins from grapes of 17° Brix. These studies also showed that a_w had an effect on color due to Maillard reactions and "sugaring", the formation, during storage, of crystalline material on the surface of the raisins, but protracted storage did not have an effect on a_w as a function of moisture content.

Near infrared diffuse reflectance spectroscopy was used by Delwiche et al. (1991) to examine starch-water and cellulose-water interactions. This work demonstrated that NIR spectroscopy could be used to analyze and describe properties of the bound water. Near infrared analysis has been used to measure a
wide array of food and agricultural products for components such as, moisture, fat, protein, sugars, and the other carbohydrates (Williams and Norris 1987). Birth et al. (1985) determined dry mater in onions. Dull et al. (1989) measured soluble solids in cantaloupe using near infrared transmittance (NIT) spectroscopy, and moisture in dried dates was also predicted using NIT (Dull et al. 1991). Because $a_w$ is strongly dependent upon moisture and soluble solids contents, it is reasonable to expect that it could be predicted through NIR analysis.

In commercial processing of sun-dried raisins, and most other dried fruit, the products are dried to a low moisture level for preservation. Final processing comprises cleaning, washing, and hydration. Raisins are initially dried to about 9-12% moisture. At these moisture levels the product is very hard and unpalatable. Final processing increases the moisture content to 16-18%, making the raisins palatable. Established moisture standards for California Seedless Raisins (Federal Register, 7CFR Part 989) limit the moisture content of the processed product to 18% or less. When used as an ingredient in baked or confectionery products, the raisins may be further hydrated before addition to the final product, in order to obtain a desired texture or other functional property.

The purpose of this research is to determine how precisely and accurately moisture content and $a_w$ may be predicted with NIR. In addition to measuring moisture and $a_w$, in order to establish value, functionality, and preservative characteristics of raisins, a rapid prediction of these two properties, to compare their relative values, may be useful to estimate and monitor their maturity quality.

All of these predictions may be useful for a statistical process control (SPC) operation. At various stages along the processing line, including preconditioning, rapid $a_w$/moisture measurements would allow operators to adjust processing parameters and blend lots to ensure that the end product would meet specifications. This would be especially useful where processors are attempting to meet specifications for specific buyers that go beyond the specification for California Seedless Raisins.

Immediately following final processing, to condition raisins for market, the product is not in equilibrium for moisture or $a_w$. The challenge is to develop a method for predicting equilibrium moisture and $a_w$, which is accurate and repeatable, based on measurements that are made on a system that is fundamentally in a nonequilibrium moisture state.

**MATERIALS AND METHODS**

**Whole Raisins**

**Sample Selection.** Samples of incoming raisins of varying moisture contents and maturity grades, preconditioned raisins from a processing plant, and processed raisins, which were purchased from several retail stores, were selected for analysis.
All samples used for NIR calibrations were in a state of complete moisture equilibrium.

**NIR Scans.** The samples were scanned in an NIRSystems 6500 (6500), equipped with a transport module and an NIRS Natural Product Cell (Foss North America, Eden Prairie, MN). The 6500 utilizes a grating a grating monochromator, and produces spectra from 400 nm to 2500 nm in 2 nm increments. The traversing speed of the sample cell was adjusted to allow 50 scans to be taken and averaged for each reload of a sample. Ten scans of a reference plate were collected and averaged before and after each sample reload was scanned. Three reloads were made of each sample. The three averaged scans were combined, and stored as a single spectrum for each sample. The spectra were stored in optical density (OD) units, log (1/R), where R is the percent of energy reflected. A total of 84 samples were scanned, representing a diverse population of moisture contents and quality grades.

Instrument operation, spectra evaluation, and calibration were made with NIRS 2, Versions 3 and 4,(NIRS2) (Infrasoft International, Foss North America, Eden Prairie, MN)

**Water Activity Measurements.** An AquaLab Model CX-2 (AquaLab) water activity meter (Decagon Devices, Pullman, WA) measured water activity per manufacturer’s instructions. The AquaLab is a dewpoint-measuring device, which measures \(a_w\) directly, with a precision of \(+/-0.003\). Distilled water and saturated salt solutions of known \(a_w\) were measured each day to verify the accuracy of the meter. The sample holder for the AquaLab is a polypropylene cup 10 mm deep and about 40 mm diameter. A single layer of whole raisins, comprising 5-8 raisins depending on their size, and weighing about 5 g, were placed in the cup for each \(a_w\) measurement. Three replications of \(a_w\) were measured for each sample.

**Ground Raisins**

**Sample Selection.** Fourteen lots of incoming raisins of varying quality grades and moisture levels were collected at incoming grading stations. The raisins were hydrated in a two-stage process. Prior to hydration 400-g aliquots of each lot were taken and placed in sealed glass jars. The samples were divided into 2 subgroups of 6 and 8 samples. The first subgroup of 6 lots was hydrated and held for 42 days before final hydration. The second subgroup of 8 lots was hydrated and held for 42 days before final hydration. The second subgroup of 8 lots was hydrated and held for 14 days before final hydration. Hydration was accomplished by immersing the raisins in distilled water for specified periods, 4, 6, and 8 min. After immersion the raisins were drained in a colander for 5 min and placed in sealed 1-gallon glass jars. The jars were turned and inverted at 1-h intervals for 3 h, to mix the raisins and promote an even distribution of moisture within samples. After 24 h the samples
were removed from the jars, thoroughly mixed by turning them from pan to pan 20 times and then placing them back in the closed jars. The same mixing procedure was performed 48 h after hydration. Prior to hydration the samples ranged in moisture from 11.9 to 20.7% (wet basis). After the initial hydration moistures ranged from 19.2 to 26.4%. Prior to final hydration, 400-g aliquots were drawn from each lot and placed in sealed glass jars. Final hydration was accomplished by immersing the samples for 0.5, 1.0, 1.5, and 2.0 min in distilled water, and draining in a colander for 5 min. Following final hydration, the samples ranged from 25.6 to 31.9% moisture wet basis.

A wide range of moisture level was used, because bakers and other users of raisins frequently further hydrate the raisins to achieve specific textural or other functional properties in processed products. Rapid measurements of raisin properties could be useful to them.

A second set of 18 samples, taken directly from the end of the processing line, was collected at a commercial raisin processing plant. Samples were collected at the official grading laboratory and placed in closed glass jars. Samples were collected from two separate processing lines at one-half hour intervals. A total of 18 samples were collected.

NIR Scans. About 250 mL aliquots were removed from the glass sample containers and ground in a food grinder (Kitchen Aid, Dayton, Ohio), fitted with an 0.45 mm perforated plate. After grinding the sample was hand kneaded to enhance uniformity.

Ground raisins were scanned in the transport module of the 6500 using an NIRS Half-Cell Cup, (Foss North America, Eden Prairie, MN) and NIRS2 was used to operate instrument and evaluate the data. A layer of plastic food wrap (Glad Cling Wrap, First Brands, Danbury, CT) was used to line the sample cup and holder, to aid clean up. All samples were scanned using the lining, to minimize its effect between scans. The reference plate was not lined with the food wrap. As for whole raisins, each scan contained 50 subscans of the sample, and 10 scans of the reference plate were taken before and after each sample scan was collected. A second scan was made of each sample by inverting the holder and repeating the procedure. The two scans were averaged and stored as a single spectrum, in log (1/R) form. A total of 98 spectra were collected.

a<sub>w</sub> Measurement. As for whole raisins, the AquaLab was used to measure a<sub>w</sub>. Immediately after scanning, two replicate samples, approximately 5 g each, were removed from the midline of the half-cell cup. Using a small spatula, the samples were evenly spread over the bottom of the AquaLab sample container. Two replicate measurements were made using two AquaLab meters. The meters were identical models, CX-2, but one was purchased in 1991 and the other in 1997.
Moisture Analysis. Two, approximately 5-g, samples were collected for moisture analysis, simultaneous with collecting samples for aw measurement. Moisture was measured by the vacuum oven method (AOAC 1984, 6 h 70 +/- 1°C, < 100 mm Hg). All moisture results were expressed in "as is" or wet-basis form.

Sampling Schedule. A schedule of hydration and sampling times was developed to provide a set of analyses that would represent a wide range of levels of moisture equilibration as well as a full range of moisture and aw values.

Commercial Samples. The commercial samples were divided into 2 subgroups. One group contained 8 samples and was analyzed 2 days after collection and 20 days after collection. The other group of 10 samples was analyzed 6 days after collection.

Hydrated Samples. Aliquots taken of all of the samples before hydration were analyzed, assuming they were fully equilibrated.

The first set of 6 samples was analyzed 40 days after the initial hydration and assumed to be fully equilibrated. They were further analyzed 1 day and 14 days after the final hydration.

The second set of 8 samples was analyzed 27 days after the initial hydration. Further analyses were made 3 h, 1 day, 5 days, and 14 days after final hydration.

RESULTS AND DISCUSSION

Spectral Characteristics

The log (1/R) spectra for a sample of incoming raisins are shown in Fig. 1. The upper curve is for whole raisins, and the lower curve is for ground raisins. The higher curve for the whole material is probably due to multiplicative scatter effects as the source radiation penetrates deeper into the sample. A set of spectra of ground raisins from the same initial lot, but hydrated to different levels, 14.3, 19.8, and 29.7% moisture shown in Fig. 2. As the degree of hydration increases the log (1/R) values increase, which is also expected as the increased moisture results in increased absorption.

A mathematical treatment, especially derivatives, of the spectra is recommended to obtain more information from them, and a second order derivative is recommended to analyze the spectra. (Hruschka 1988). The second derivative is used because it presents absorption peaks in the same location as they appear in the log (1/R) spectrum, but they are pointing down rather than up. The NIRS2 program is extremely versatile and comprehensive for analyzing and calibrating NIR data. It contains routines for developing numerous types of derivative spectra. The
derivatives are usually calculated as difference, or gap, derivatives (Hruschka 1988), expressed as: order, gap, first smooth, and second smooth. A 2,2,2,1 derivative is a second order derivative, calculated over a 2 data-point gap smoothed over 2 data-points, with no second smooth. Figure 3 shows the spectra of Fig. 2 converted to second derivative 2,2,2,1, form. Expanded views of the spectra from 892 nm to 1588 nm and from 1608 nm to 2140 nm are shown in Fig. 4 and 5, respectively. High water absorption bands usually occur at about 960 nm, 1150 nm, and 1900-2000 nm, and these bands are apparent in Fig. 3. An additional strong band appears at about 1425 nm, which corresponds with absorption by sugars. In second derivative form, the peak amplitudes are greater for the hydrated raisins up to about 1300 nm. At higher wavelengths, the amplitudes are greater for the drier raisins. This is probably due to differences in the width of the bands, because narrower bands would be expected to have greater amplitudes in the second derivative. There appears to be little shift in the band locations due to hydration, except in the regions from about 1300 nm to 1500 nm and from 1800 nm to 1950 nm, where the peaks for the drier raisins are shifted about 20 nm higher.
The standard deviation of the second derivative spectra is shown in Fig. 6. The regions with the largest standard deviations correspond to the major absorption bands. This is due to the fact that the major absorption regions correspond to moisture absorption bands. Because moisture level is the primary variable among the samples, the standard deviation is greatest in these regions.

\textbf{\textit{a}}_{\text{w}} \text{ and Moisture Measurements}

Analysis of variance (SAS, v 6.1, SAS Institute, Inc., Cary, NC) was applied to the \textit{a}_{\text{w}} and vacuum oven moisture analyses. The root mean square error (RMSE) for \textit{a}_{\text{w}} is 0.00489, and the mean (M) of the population is 0.63025. This results in a coefficient of variation (CV) of 0.776\% where the CV is calculated as (RMSE)/(M)*100. For the vacuum oven moisture measurements, the RMSE is 0.26197, and the M is 22.0795, resulting in a CV of 1.154\%. 

\textbf{FIG. 2. ABSORPTION SPECTRA, AS LOG (1/R) VERSUS WAVELENGTH, IN THE RANGE OF 400 TO 2492 NANOMETERS, FOR A SAMPLE OF GROUND RAISINS AT THREE LEVELS OF HYDRATION}
The higher CV for moisture is probably due to the larger number of measurements and the additional preparation procedures that must be made for vacuum oven analyses, compared to $a_w$. Sampling error should be the same for both analyses, as sample size and sampling procedure were the same for both measurements. The $a_w$ measurement by the AquaLab requires only placing a layer of material across the bottom of the sample cup. No preparation or precise weight measurements are needed. The vacuum oven moisture method requires an initial tare weight, an initial total weight, an initial total weight, and a final total weight. Samples must be ground with sand and predried over steam for the vacuum oven analysis. All of the weight measurements and the preparation operations are potential sources of error between replicates. The moisture error should be $\pm 0.2\%$ (AOAC 1984). While the error in this study is slightly higher, the CV for moisture would still exceed that for $a_w$ if the error were within the reported limits.

The $a_w$ of whole raisins as a function of time after hydration was measured for 6 lots of raisins, and the results are shown in Fig. 7, for laboratory hydrated raisins. As expected, $a_w$ decreases with time as the water penetrates and reaches equilibrium.
within the individual raisins. Prior to reaching equilibrium the values fluctuate unevenly due to the presence of capillary-held water on the surface. Even ground raisins have an elevated $a_w$ immediately after processing, but the values at 2 and 20 days are essentially identical.
FIG. 5. THE SECOND DERIVATIVE OF LOG (1/R) ABSORPTION SPECTRA IN THE RANGE OF 1608 TO 2140 FOR GROUND RAISINS AT THREE LEVELS OF HYDRATION

TABLE I.
WATER ACTIVITY OF EIGHT LOTS OF RAISINS MEASURED AT FOUR TIME PERIODS AFTER HYDRATION

<table>
<thead>
<tr>
<th>Lot No.</th>
<th>3 Hours</th>
<th>1 Day</th>
<th>5 Days</th>
<th>14 Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.735</td>
<td>0.735</td>
<td>0.734</td>
<td>0.735</td>
</tr>
<tr>
<td>2</td>
<td>0.763</td>
<td>0.757</td>
<td>0.760</td>
<td>0.762</td>
</tr>
<tr>
<td>3</td>
<td>0.706</td>
<td>0.705</td>
<td>0.708</td>
<td>0.704</td>
</tr>
<tr>
<td>4</td>
<td>0.728</td>
<td>0.728</td>
<td>0.723</td>
<td>0.726</td>
</tr>
<tr>
<td>5</td>
<td>0.713</td>
<td>0.720</td>
<td>0.712</td>
<td>0.713</td>
</tr>
<tr>
<td>6</td>
<td>0.724</td>
<td>0.714</td>
<td>0.718</td>
<td>0.717</td>
</tr>
<tr>
<td>7</td>
<td>0.712</td>
<td>0.693</td>
<td>0.703</td>
<td>0.701</td>
</tr>
<tr>
<td>8</td>
<td>0.696</td>
<td>0.693</td>
<td>0.696</td>
<td>0.697</td>
</tr>
</tbody>
</table>

1 Water activity measured after raisins were ground.
FIG. 6. THE STANDARD DEVIATION OF THE SECOND DERIVATIVE OF THE LOG (1/R) SPECTRAL FOR THE GROUND RAISIN POPULATION

TABLE 2.
WATER ACTIVITY OF FIVE LOTS OF COMMERCIALY PROCESSED RAISINS MEASURED AT THREE TIME PERIODS AFTER PROCESSING

<table>
<thead>
<tr>
<th>Sample NO.</th>
<th>Whole</th>
<th>Ground</th>
<th>Ground</th>
<th>Ground</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.792</td>
<td>0.628</td>
<td>0.579</td>
<td>0.575</td>
</tr>
<tr>
<td>2</td>
<td>0.712</td>
<td>0.64</td>
<td>0.568</td>
<td>0.564</td>
</tr>
<tr>
<td>3</td>
<td>0.774</td>
<td>0.631</td>
<td>0.535</td>
<td>0.537</td>
</tr>
<tr>
<td>4</td>
<td>0.867</td>
<td>0.619</td>
<td>0.543</td>
<td>0.541</td>
</tr>
<tr>
<td>5</td>
<td>0.828</td>
<td>0.631</td>
<td>0.543</td>
<td>0.542</td>
</tr>
</tbody>
</table>
NIR Calibrations

NIR calibrations were made for $a_w$ of whole and ground raisins and for moisture of ground raisins. The sample populations for neither the whole nor ground raisins was sufficient to establish a calibration that could be used to predict the $a_w$ or moisture values in future spectra; however, for the purposes of this work, they can be used to assess the kinds of populations that must be used to develop a suitable prediction model.

Whole spectrum calibrations were made using the calibration program of NIRS2.

Modified Partial Least Squares (MPLS) was used to correlate the spectral and measured data, $a_w$ and moisture. The spectra were first converted to first derivative, 1,4,4,1 form. While second order derivative spectra are convenient to interpret and analyze the spectra, the first order derivative appeared to calibrate as well. Using lower order derivatives for calibration probably minimizes the effects of noise in the spectra. The correlation between the first derivative spectra and the $a_w$ and moisture for ground raisins is shown in Fig. 8.
Because moisture content is a very large component of the \( a_w \) value, it is expected that the two parameters will have very similar correlation with spectral values. While the correlation is almost identical for both parameters, the correlation is slightly higher for \( a_w \) compared to moisture for most regions of the spectra.

Cross validation was used to measure the precision of the calibration. The calibration program calculates 2 parameters, the standard error of cross validation (SECV) and one minus the variance ratio (1-VR). The variance ratio is calculated as \((\text{SECV})^2/\text{SD})^2\), where SD is the standard deviation of the reference sample population. The (1-VR) parameter is similar to the adjusted \( R^2 \), statistic associated with standard error (Stone 1974).

Figure 9 shows the predicted values of \( a_w \) for whole raisins plotted against the measured values. This calibration had a SECV of 0.0142, and a (1-VR) of 0.971.
All 84 scans were used in the calibration. No outliers were removed, and the calibration was optimized with only 3 PLS terms. It is obvious that two sub-populations are contained in the samples, below $a_\omega$ of about 0.53 and above $a_\omega$ of 0.58. The correlation between predicted and measured value appears similar for both subpopulations.

The calibration results for $a_\omega$ of the ground raisins are shown in Fig. 10. For this calibration the SECV is 0.006 and (1-VR) equal to 0.996, indicating a very high correlation between measured and predicted results, as well as a very low standard error. In this case the calibration was optimized at 9 PLS terms.

When the calibration was restricted to the spectral region of 800 nm to 1100 nm, where relatively cheap silicon detectors are used, the correlation remained quite high, (1-VR) equal to 0.985, but the standard error, SECV, doubled to 0.012.

The lower SECV for ground raisins compared to whole raisins is probably due to the fact that ground raisins are not affected by surface variations of the samples. Whole raisins have various amounts of wax and "bloom" on the surface which may affect the spectra and the measured $a_\omega$ values. The AquaLab operates in a cyclical manner, and when the difference in $a_\omega$ between cycles becomes less than 0.001, the
result is given. Surface waxes act as a partial barrier to vapor transfer, and may result in a premature conclusion of the test. The surface conditions of the raisins may also affect the spectra in ways that do not relate to $a_w$. Full spectra calibrations may overcome many of the affects on spectra, but any effects of reduced precision in the reference method cannot be compensated.

Results of the moisture calibration are shown in Fig. 11. It is obvious the calibration for moisture is not as precise as the calibrations for $a_w$. The calibration optimized at 4 PLS terms, with SECV equal 0.689 and (1-VR) equal to 0.985. The relatively high SECV for moisture compared to $a_w$ may be due to several factors. Errors in the primary vacuum oven measurements, as previously mentioned, would lower calibration precision. This could be overcome by increasing the number of replicate measurements. Also, vacuum oven drying may remove volatile substances other than water. If the additional volatile materials removed were not directly proportional to the water vapor removed, the calibration would be less precise.
The higher levels of moisture in these samples represent extreme moisture conditions for stored raisins. Even though microbiological spoilage does not occur, chemical modifications may be occurring that increase the quantities of water and other volatile substances that may be removed by vacuum drying. In our earlier work (Huxsoll et al. 1995a) we obtained a standard error for raisin moisture of about 0.3%. That analysis utilized near infrared transmittance (NIT), and the population was entirely incoming raisins that had not been hydrated. To improve precision, separate calibrations should be made for incoming and hydrated raisins, but using a reference analysis, such as the Karl Fischer analysis, which only measures water, would be the preferred approach.

The polynomials (Bolin 1980) relating moisture and $a_w$ are:

- Moisture = 36.60 - 122.5($a_w$) + 144.3($a_w$)$^2$, for raisins from 17° Brix grapes, and
- Moisture = 39.30 - 126.9($a_w$) + 146.5($a_w$)$^2$, for raisins from 22° Brix grapes.

At $a_w$ of 0.60, the moisture content of the low-grade raisins would be 15.05% and the high-grade raisins would be 15.90%. With a standard error of 0.689% in
the moisture prediction it would not be possible to discriminate between the two grades based on their water activity to moisture relationships. The polynomials were based on \( a_w \) values measured to the nearest 0.01, which corresponds to a difference of about 0.2% moisture. If the standard error in the moisture calibration could be reduced to 0.2%, the predicted moisture and predicted \( a_w \) could be compared to give a broad assessment of quality.

**CONCLUSIONS**

This research has shown that NIR has very good potential to measure water activity in raisins that are in a nonequilibrium moisture condition, and the predictions may be made within a few hours of hydration. Further work should be done with ground raisins. Collecting spectra immediately after hydration and measuring \( a_w \) about one week after hydration should make calibrations that would predict equilibrium \( a_w \) from spectra taken immediately after hydration. A single full-spectrum calibration appears to be satisfactory for making \( a_w \) predictions for the entire range of moisture content that is of practical interest. The AquaLab dewpoint device is a very reproducible, accurate reference which leads to precise prediction calibrations.

The calibration for moisture lacked precision, probably due to errors in the vacuum oven reference method, and to a very poorly structured reference population for moisture calibration. Based upon previous NIR moisture analyses for raisins and other products, the precision can be substantially improved by properly structuring the reference population, but improving the reference method could make even further improvement.

A distinct advantage of NIR analysis is that once a spectrum is collected predictions may be obtained for all of the properties of the sample for which a calibration exists. Although no general specification exists for water activity in the grade standards for raisins, it may be an important property for some users. The ability to predict \( a_w \) simultaneously with other properties may be useful for assessing the overall quality of the product.

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