APPLICATION NOTE

FT-NIR Spectroscopy

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Detecting Quinoa Flour Adulteration Using FT-NIR Spectroscopy

Introduction

Quinoa production has been increasing rapidly in the past few years as more people worldwide have begun to incorporate the highly nutritional grain into their diets.[1] Among other health benefits, including high levels of fibre and protein, quinoa and quinoa flour can provide gluten-free alternatives to usual wheat-containing products.[2]

Quinoa flour is a high-value product and, therefore, susceptible to adulteration with lower-value flours, allowing unscrupulous suppliers to increase their profits. More worryingly, suppliers may use gluten-containing flours for adulteration whilst still marketing the product as suitable for consumers with gluten intolerances. Fourier Transform Near-Infrared Spectroscopy (FT-NIR) provides a quick and easy method to determine the identity and concentration of any adulterants present in quinoa flour.

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Experimental

NIR spectra of pure quinoa flour and five possible adulterant flours were collected on a PerkinElmer Spectrum Two N™ FT-NIR spectrometer. A 100 mm Petri dish was filled with the sample, placed on a Near Infrared Reflectance Module (NIRM) and scanned using the parameters shown in Table 1. A sample spinner was used to allow a larger surface area to be scanned, resulting in more representative and reproducible sampling. 15 spectra of pure quinoa flour (five replicates from three different commercially available brands) and one spectrum of each adulterant (buckwheat flour, corn flour, rice flour, soya flour and white flour) were collected.

Figure 1. PerkinElmer Spectrum Two N with Near Infrared Reflectance Module.

Table 1. Scanning parameters for analysis of quinoa flour and adulterant flours.

Scanning Parameters	
Spectral Range	10,000-4,000 cm^{-1}
Resolution	16 cm^{-1}
Number of Scans	32

Additionally, 17 pure quinoa samples were spiked with each adulterant over a range of concentrations from 2-95% (w/w). Spectra of each of the adulterated quinoa flour samples, 100% quinoa flour and 100% adulterant were collected and used to create a quantitative calibration. The samples were split such that 16 spectra were used for calibration and three were used for independent validation of the model. Cross validation was also carried out for all models, using the Leave-1-out method.

A Partial Least Squares (PLS1) calibration model was built for each of the adulterant flours using PerkinElmer Spectrum Quant™ software. Table 2 shows the pre-processing parameters used on the spectra in each model.

PLS1 Calibration Models

Figure 2 shows an example correlation plot for the corn flour model, including the calibration and independent validation data points. The data points are evenly distributed about the unity line, showing there is a good level of correlation between the specified concentration of adulterant and the concentration predicted by the model.

Table 3 highlights the regression data of all the calibration models. The R^2 values range between 98.9-99.9% which further indicates the high level of agreement between the specified and predicted concentrations of adulterant flour, especially for corn flour. Table 4 shows the average independent validation results for the models. The standard errors of prediction (SEP) lie in an acceptable range, with soya flour showing a particularly good level of correlation. In order to improve the models, a greater number of samples could be used to create the calibrations.

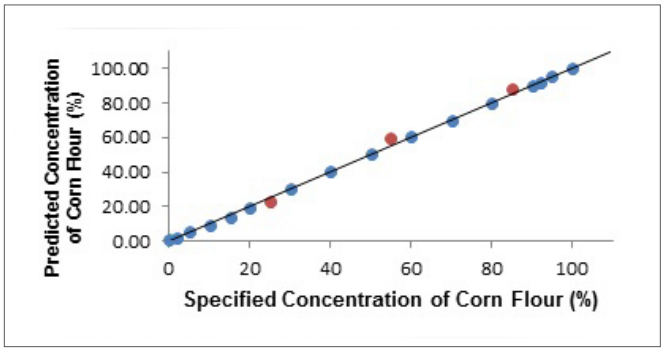

Figure 2. Correlation plot for corn flour model showing calibration (blue) and validation (red) data points with the solid black line indicating the unity line.

Table 2. Pre-processing parameters for adulterant quinoa flour models.

Adulterant Flour	Range	Normalization	Baseline Correction	
			Derivative Order	Noise Reduction
Buckwheat	9000-4000 cm^{-1}	MSC	First	Medium
Corn	10000-4000 cm^{-1}	MSC	First	Light
Rice	9000-4000 cm^{-1}	SNV	First	Medium
Soya	9000-4000 cm^{-1}	MSC	First	Light
White	9000-4000 cm^{-1}	MSC	First	Medium

Table 3. Regression summary for adulterant flour models (where SEC is the standard error of calibration, SEP is the standard error of prediction, and CVSEP is the cross validation standard error of prediction).

Adulterant Flour	Number of PCs	R^2	SEC (%)	SEP (%)	CVSEP (%)
Buckwheat	1	98.911	3.968	4.041	4.509
Corn	3	99.982	0.548	0.789	2.431
Rice	2	98.937	4.068	4.241	4.434
Soya	1	98.872	4.039	4.105	4.258
White	5	99.805	1.985	2.167	3.128

Table 4. Independent validation results from adulterant flour models.

Adulterant Flour	Average True Sample Property Value (%)	Average Predicted Sample Property Value (%)	SEP (%)
Buckwheat	55.00	58.71	4.869
Corn	55.00	56.84	3.295
Rice	55.00	52.31	3.458
Soya	55.00	55.47	1.695
White	55.00	55.88	3.346

Adulterant Screen

The Adulterant Screen™ algorithm is a semi-targeted approach used to detect, identify and semi-quantitatively estimate the level of adulterant present in a sample, without needing to run quantitative calibration standards. The user simply needs to generate a library of unadulterated material spectra with as much natural variation as possible, such as samples from different batches or suppliers. Then, single scans of each adulterant of concern must be compiled into an adulterant library; new adulterants can be continually added to the library when required.

When a sample is scanned, the algorithm compares it to a PCA model created from the unadulterated material library and produces a residual spectrum, indicating the part of the spectrum that cannot be explained by the model. Adulterant Screen then adds each adulterant, in turn, into the model. If the residual decreases for a particular adulterant, this indicates the adulterant is present in the sample. Figure 3 shows the observed residuals from analysis of 20% cornflour adulterated sample.

An Adulterant Screen method was created by inputting all 15 spectra of pure quinoa flour as 'material spectra' and using the spectra of each of the five pure adulterants as 'adulterant spectra'. The method was then tested using quinoa flour samples spiked with known levels of adulterants. The spectra were pre-processed using a first derivative baseline correction and adjusting the spectral range to 9,000-4,000 cm^{-1}. The results are shown in Table 5.

In all cases, except pure quinoa flour, the adulterated samples generated a "Fail" result, signifying the presence of an adulterant. The Adulterant Screen method also correctly identified the adulterant flour present and gave an estimated level of that adulterant. In some cases, underestimates and overestimates of the levels of adulterant present occurred. However, this method is only intended as a quick screening technique, and failed samples could be sent for confirmatory testing if required.

Adulterant Screen can also be used within Spectrum Touch™ methods to provide a simple interface for use by routine operators. Figure 4 shows the Spectrum Touch Workflow correctly identifying the adulterant flour present. More detailed results are also provided, indicating the estimated level of the adulterant.

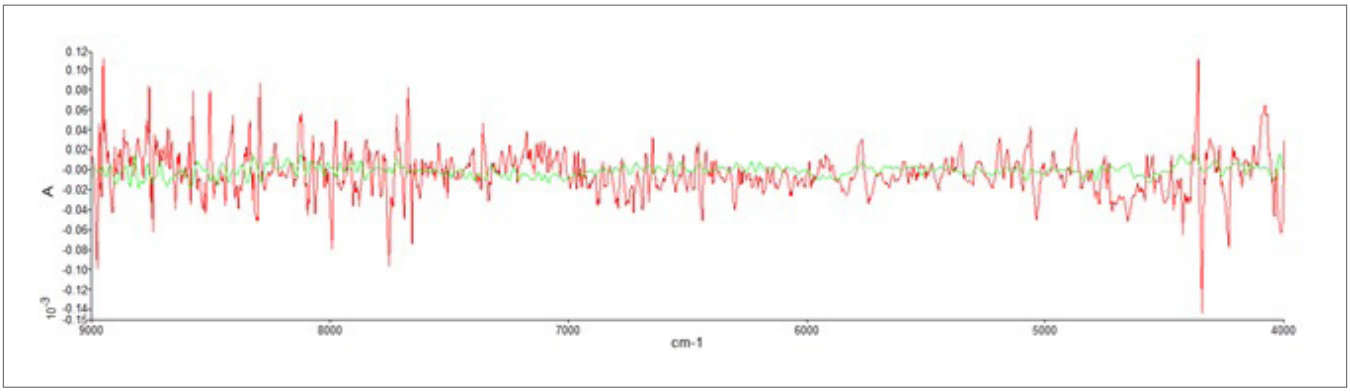

Figure 3. Spectral residuals before (red) and after (green) fitting adulterants.

Table 5. Adulterant Screen results for a series of adulterated quinoa flour samples.

Sample Name	Level (%)	Detection Limit (%)	Adulterant Screen Pass/Fail
Buckwheat Flour (20%)	13.4	2.01	Fail
Buckwheat Flour (10%)	9.28		Fail
Corn Flour (20%)	43.34	0.82	Fail
Corn Flour (10%)	14.32		Fail
Rice Flour (20%)	11.34	1.67	Fail
Rice Flour (10%)	7.94		Fail
Soya Flour (20%)	25.62	0.28	Fail
Soya Flour (10%)	12.92		Fail
White Flour (20%)	23.35	1.11	Fail
White Flour (10%)	16.37		Fail
Quinoa Flour (100%)	-	-	Pass

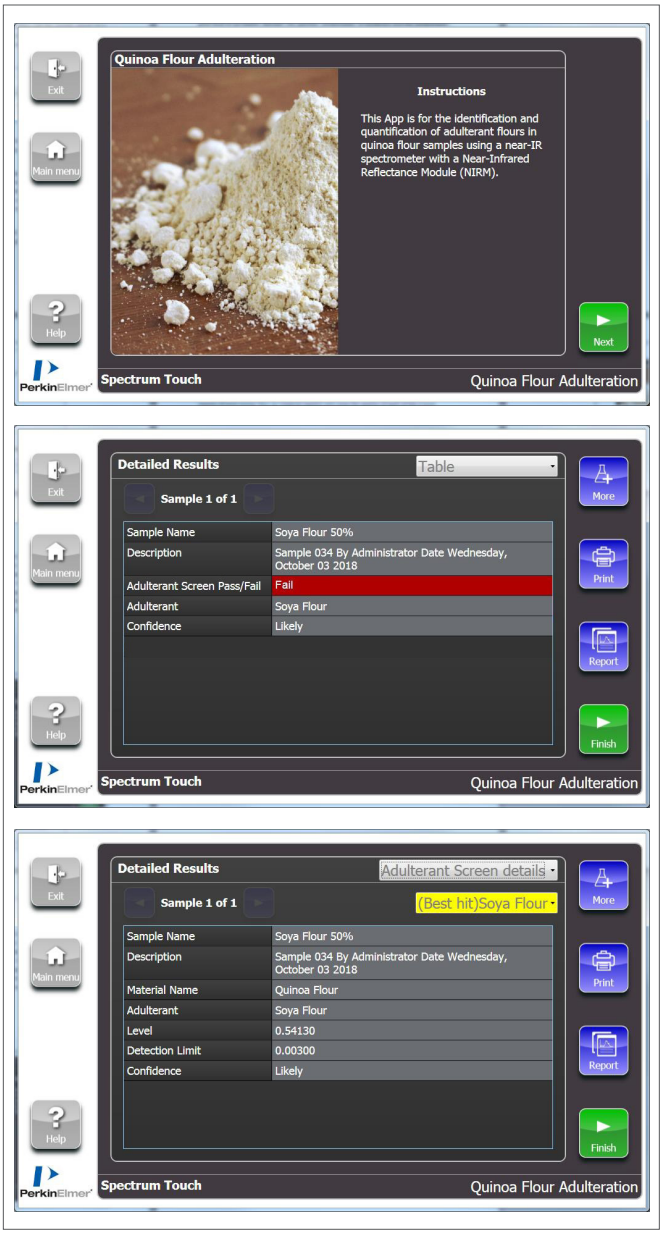

Figure 4. Example of Spectrum Touch Workflow and Adulterant Screen results for quinoa flour adulteration.

Conclusion

The results show that NIR spectroscopy provides an effective and rapid technique for detecting quinoa flour adulteration. PLS modelling provides good sensitivity in quantifying adulterant levels present in a sample but the method is time-consuming as separate calibrations are required for each adulterant. Adulterant Screen, on the other hand, provides quick identification and quantitative estimation of adulterant levels present in the sample. Only one spectrum of each adulterant is required and new adulterants can be added to the model at any time. These methods can also be deployed in Spectrum Touch software, providing an easy-to-use analysis technique with step-by-step instructions.

References

1. Quinoa production worldwide from 2010 to 2016 (in metric tons), Statista, 2016.
2. A. Bjarnadottir, Quinoa 101: Nutrition Facts and Health Benefits, Healthline, 2015.

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