APPLICATION NOTE

FT-IR NIR Spectrometry

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Determination of Levels of Spice Adulteration using Near-infrared Spectroscopy

Introduction

Since the late 1800's scientists have been testing spice samples and discovering that they are adulterated. Some spices are high-value products that can be adulterated with lower-value commodities for commercial gain by unscrupulous suppliers. Some common adulterants of spices range from talc powder, ground walnut shells, cassia bark and sand, to wheat starch, saw dust, millet, buckwheat, and cornstarch. Commonly adulterated spices include garlic powder, black pepper, and cinnamon. Fourier Transform Near-Infrared Spectroscopy (FT-NIR) is shown here to be an effective and rapid technique to determine if these types of spices have been adulterated.

Method

Samples of pure cinnamon, garlic powder, and black pepper were measured along with samples of some pure adulterants, namely talc, corn starch, and millet. Adulterated samples of the spices were prepared to demonstrate the applicability of the method. Near-infrared spectra were recorded using a PerkinElmer Frontier™ FT-NIR spectrometer equipped with a NIRA II sampling accessory. The powders were placed into petri dishes and placed on the NIRA II sample spinner accessory for the FT-NIR. Spinning the sample during data collection balanced out any inhomogeneity within the sample. Spectra were collected using 32 scans, at 8 cm^{-1} resolution, from 10,000 cm^{-1} to 4,000 cm^{-1}. Multiple independent spectra were collected for each of the spice types in order to build a model representing expected variation for that sample type. A model was created using a Soft Independent Modelling by Class Analogy (SIMCA) approach and also Adulterant Screen™ to discover if adulterated spice samples could be distinguished from a pure sample.

Results

FT-NIR spectra obtained for the pure spices are shown in Figure 1. The spectra of these materials in the near-infrared region have broad peaks showing first overtones and combination bands of the fundamental vibrations in the mid-infrared region of the spectrum. The replicate spectra measured for these materials were used to develop a SIMCA model that could be used for raw material identification or quality testing.

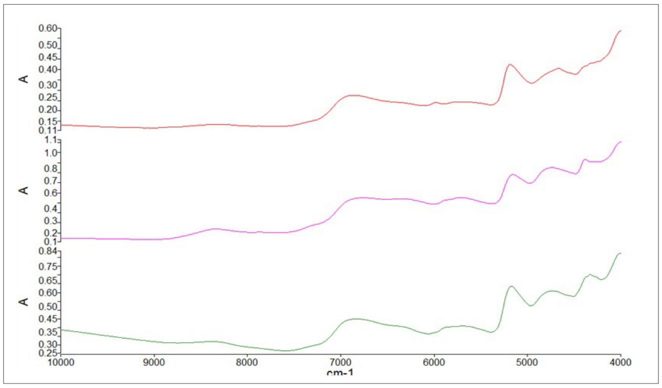


Figure 1. Spectra of the pure spices : Cinammon (red), Garlic Powder (purple), and Black Pepper (green).

The three-dimensional representation of this SIMCA model is shown as Figure 2, showing clear separation of the different classes of materials in the model for the pure materials. Using this model it would be easily possible to classify an unknown sample of any of these pure spices.

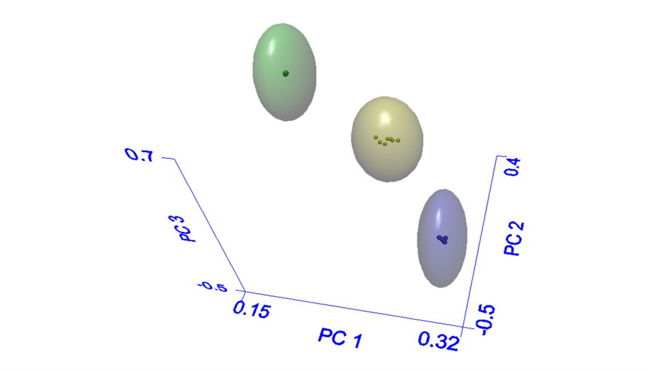


Figure 2. SIMCA model for pure spice samples: Cinnamon (top left), Black Pepper (middle), and Garlic Powder (bottom right).

FT-NIR spectra of three of the adulterants commonly encountered within spice samples are shown in Figure 3. Corn starch and millet have similar broad spectra to those observed in the spectra of the pure spices. Talc has some unique, sharp spectral features that can make detection of its use easier.

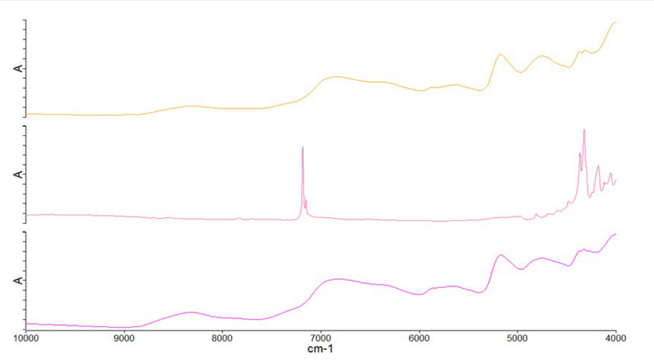


Figure 3. Spectra of the adulterants in this study: Corn Starch (top), Talc (middle), Millet (bottom).

A pure garlic powder sample was adulterated with a 10 % spiked amount of talc in order to test both the SIMCA model and an Adulterant Screen method. The spectrum of the pure garlic powder and the 10 % talc-spiked sample are shown in Figure 4. The spectral features due to the talc are highlighted in this Figure, showing clear differences from the pure sample.

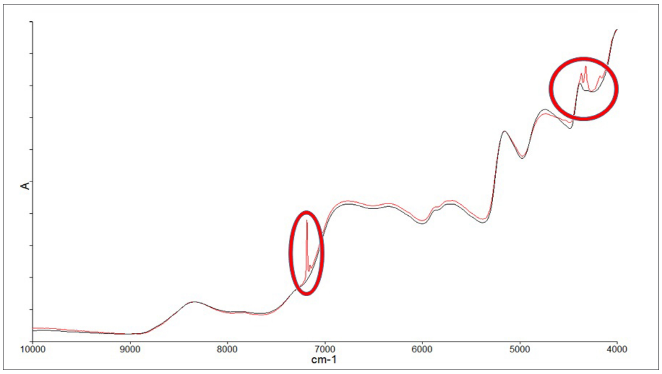
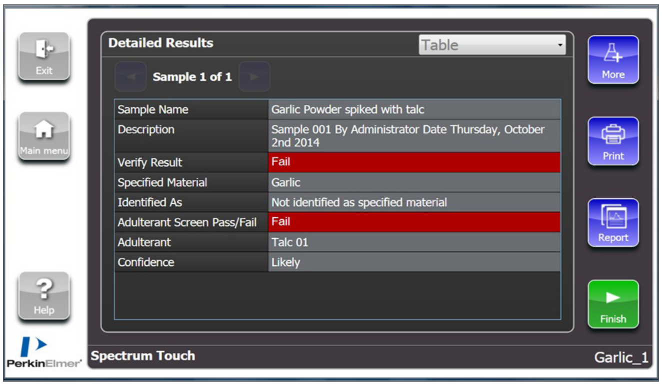


Figure 4. FT-NIR overlay of garlic powder spectrum with talc adulterant.

A Spectrum Touch™ method with a simple user interface was created to include both the SIMCA model and the Adulterant Screen method for the garlic powder. The spiked sample was tested against these methods to determine whether the adulteration would be detected. The results' screen is shown as Figure 5.



Sample Name	Garlic Powder spiked with talc
Description	Sample 001 By Administrator Date Thursday, October 2nd 2014
Verify Result	Fail
Specified Material	Garlic
Identified As	Not identified as specified material
Adulterant Screen Pass/Fail	Fail
Adulterant	Talc 01
Confidence	Likely

Figure 5. Example results for garlic Adulteration Screen with SIMCA from Spectrum Touch.

If the spectrum being measured does not conform to the rest of the spectra in the model then Verify™ (using the SIMCA algorithm) will fail the material. In this case, the spiked sample fails the Verify test. However, Verify can only inform the user that the sample has failed and cannot give any indication as to the adulterant present. In this case, the Adulterant Screen method also generates a fail result, but Adulterant Screen is able to inform the user which type of adulterant is present, correctly identified as talc.

A cinnamon sample was similarly spiked with an adulterant, in this case 10 % of corn starch. The Near-infrared spectra of cinnamon and corn starch are very similar and the differences cannot be seen easily in the absorbance spectra. However, applying a second derivative processing to the data does highlight the small differences as shown in Figure 6.

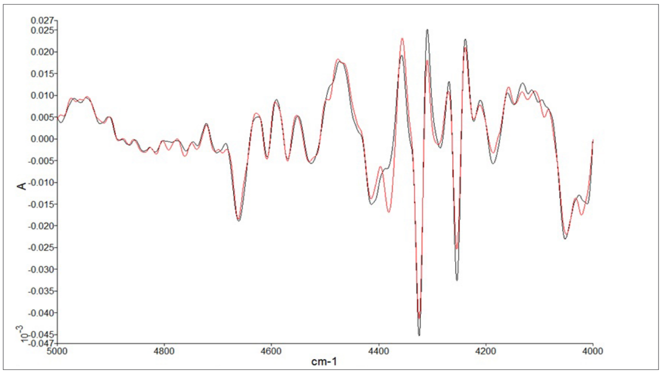
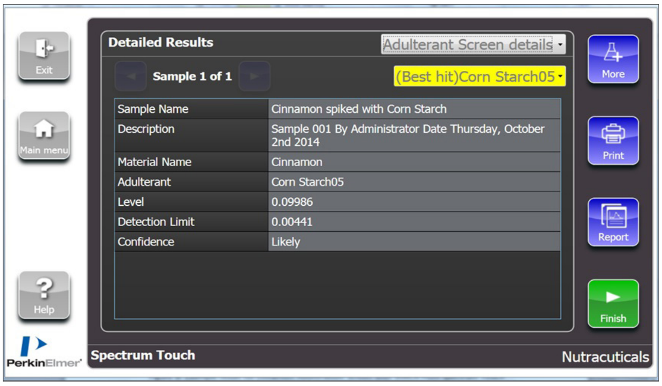


Figure 6. Second derivative spectra of pure cinnamon (black) and cinnamon spiked with Corn Starch (red).

These small differences are sufficient for the detection of corn starch as an adulterant. The same mathematical approach, as used for the garlic powder samples, was deployed for this spiked sample. Again, the Verify (SIMCA) and Adulterant Screen both generated fail results. Once the results are generated, it is possible to look at them in greater detail. Figure 7 shows the detailed results from Adulterant Screen.



Sample Name	Cinnamon spiked with Corn Starch
Description	Sample 001 By Administrator Date Thursday, October 2nd 2014
Material Name	Cinnamon
Adulterant	Corn Starch05
Level	0.09986
Detection Limit	0.00441
Confidence	Likely

Figure 7. Example results from Spectrum Touch highlighting the 'Adulterant Screen details' view for a cinnamon sample adulterated with 10% corn starch.

Not only does Adulterant Screen correctly identify the adulterant, it will also give a quantitative estimate of the level of adulterant present. This sample is reported as having corn starch present at 9.986 % for a 10 % spiked sample.

For the final spice sample in this study, black pepper, a series of dilutions were made using millet in order to generate a quantitative calibration for these mixtures. The mixtures ranged from pure black pepper containing no millet, up to 100 % millet. The spectra were measured, pre-processed using the second derivative format, then used as calibration standards within the Spectrum Quant™ package using a Partial Least Squares (PLS) algorithm. The calibration line generated is shown as Figure 8.

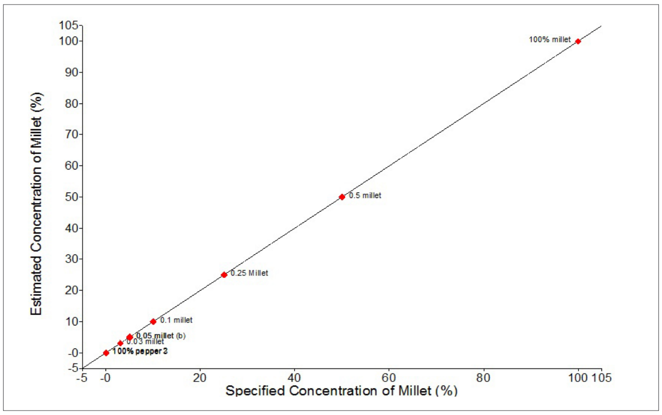


Figure 8. PLS Calibration for millet in black pepper.

The calibration shows excellent correlation between the specified and estimated concentrations of the mixtures. A small number of validation samples were used to test the quantitative method.

These same validation spectra were tested using an Adulterant Screen method for black pepper. Creating the Adulterant Screen method simply required spectra of the pure spice and the spectrum of the pure adulterant to be scanned and input into the method. Quantitative standards are not required. The spiked samples correctly failed the Adulterant Screen test. Table 1 shows the quantitative results obtained for the Validation samples using both Quant (PLS) and Adulterant Screen.

Table 1. Quantitative estimates of adulterant levels in Validation samples.

Sample	Adulterant Screen	PLS Prediction
3 % Millet	3.370	2.9834
10 % Millet	9.924	10.01
25 % Millet	22.781	24.997

These results show good levels of accuracy and a correlation between the Quant and Adulterant Screen results. The Adulterant Screen method did not require the preparation and measurement of calibration standards, thus speeding up the method development. If cases of new adulterants are uncovered, then updating the Adulterant Screen method would simply require the spectrum of that adulterant to be scanned and added to the method. A PLS method for a new adulterant would require complete re-calibration with a new set of standards.

Conclusion

FT-NIR with an Adulterant Screen is an effective way to detect adulteration of spice samples. A Verify (SIMCA) model provides sample identities with high levels of confidence and can detect when the sample does not conform to the model spectra. Additionally, Adulterant Screen can detect and identify the adulterants and predict concentrations without the need for lengthy calibration processes.

References

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