Near infrared analysis of mentholated tobaccos

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Introduction

Menthol is added to tobacco to provide a cooling effect for the smoker. Currently used laboratory methods for menthol analyses are both time consuming and labour intensive,[1] and they are not suitable for process monitoring and control. To provide a rapid analyses tool, Analytical Spectral Devices, Inc. developed a near infrared (NIR) reflectance spectroscopy method to measure menthol concentration. The technique involved the use of a portable NIR spectrometer coupled with a reflectance type fibre-optic probe.

There are more than two thousand chemical compounds in tobacco samples and there are many varieties of tobaccos.[2] Chemical analysis needs to be well established throughout the manufacturing process to regulate final product composition, concentration and formulation. Any abnormality not rapidly detected in a manufactory plant will result in either waste of the whole batch of product or suspension of the shipment. For this reason, process monitoring and analysis are very critical for quality control. Often conventional laboratory analysis is tedious and time consuming. The NIR spectroscopy method has gained a favourable reputation by providing rapid analysis, and eliminating the need for sample preparation. Thus, the process is extremely cost-effective. Non-invasive sampling and simultaneous multicomponent analysis make NIR an attractive measurement technique in many applications,[3] including the tobacco industry. Many researchers have developed classification models to differentiate the types of tobaccos as well as quantification models to measure chemical components, such as sugar, nicotine, total nitrogen, citric acid, oxalic acid, malic acid, potassium, calcium and ash. The success of this method depends on many factors, such as particle size, tobacco types, temperature variations, sample presentation.

In this study we chose mentholated tobaccos as a model system for testing the feasibility of NIR reflectance spectroscopy to measure menthol concentrations. During the cigarette manufacturing process, menthol is added to give a cooling effect. Because of taste and health concerns, the menthol level has to be controlled within a certain concentration range.[4] In this study, NIR reflectance measurement has been employed, and the results show the capability of this method to perform well for rapid on-line analysis.

Materials and methods

During the cigarette manufacturing process, about 10 lbs of cut tobacco was sprayed with a dissolved menthol solution. After mixing very well in a rotating mixer, samples were taken for laboratory analysis and other samples were collected for NIR reflectance measurements. Reflectance spectra were taken on tobacco samples using ASD's portable NIR spectrometer, ranging from 1000 nm to 1800 nm. The experimental configuration is shown in Figure 1. Two 50 watt DC tungsten lamps were used as external light sources and mounted about 14 inches away from the tobacco samples. A reflectance fibre-optic probe was fixed about one inch above the sample. This

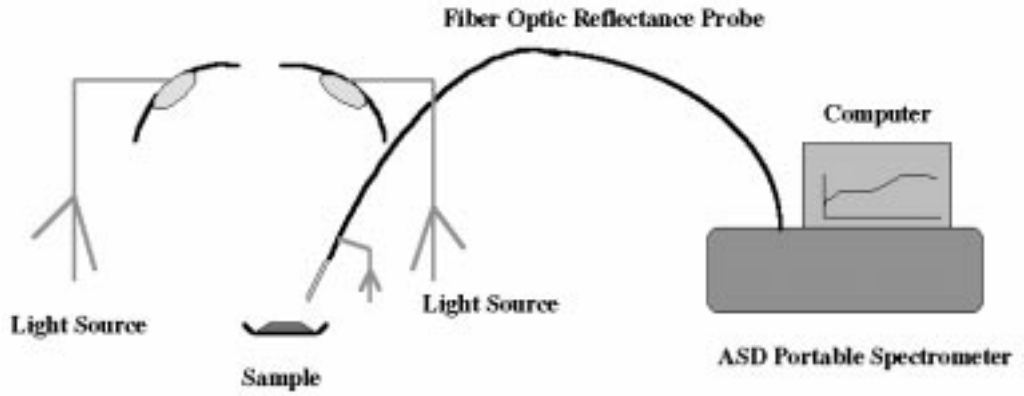

Figure 1. Schematic diagram of NIR reflectance of mentholated tobacco.

collected light from a relatively large sampling area. Five spectra on different locations of the sample were collected to average and reduce the sampling error. It takes 0.1 second to scan a single spectrum. Each spectrum of tobacco sample were recorded at 1 nm interval using the average of 50 scans each. The more spectra that can be averaged together, the better signal-to-noise ratio is obtained.

Results

Reference values of menthol concentrations were obtained by GC analysis after extracting menthol from the mentholated tobaccos. Then the tobacco was oven dried and weighed. The percentage of menthol was obtained by taking the ratio of weight of menthol to the weight of dry tobaccos.

Data preparation

All the reflectance spectra were converted to pseudo-absorbance spectra by taking log(1/*R*) transformation.

The raw log (1/*R*) spectra of tobacco samples are shown in Figure 2. For some data types, our ability to extract meaningful information can be enhanced by transforming the data prior to data analysis. Both first derivative and second derivative transformations have been tried on these spectral data. From the calibration results, we found that the first derivative transformation gave a smaller standard error of calibration. Therefore, for this data set, a first derivative transformation was performed on each spectrum to remove baseline offset due to the instrument drift and light scattering from the samples.

Calibration

After outliers were removed, the calibration set contained 15 samples. Figure 3 shows the results from the principal component regression (PCR) and partial least squares (PLS) calibration method. The models used all the sample spectra and known concentrations obtained from the reference method. Five factors were chosen based on the cross-validation results. After development, the model was applied to predict the concentration of each sample. In this figure, the x-axis is the concentration measured by GC and weighing, and the y-axis the concentration predicted by the PCR and PLS calibration model.

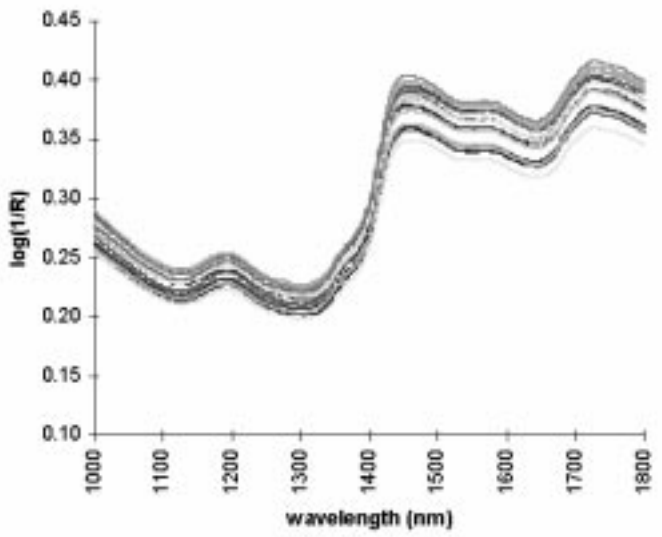

Figure 2. Pseudo-absorbance spectra of mentholated tobacco samples.

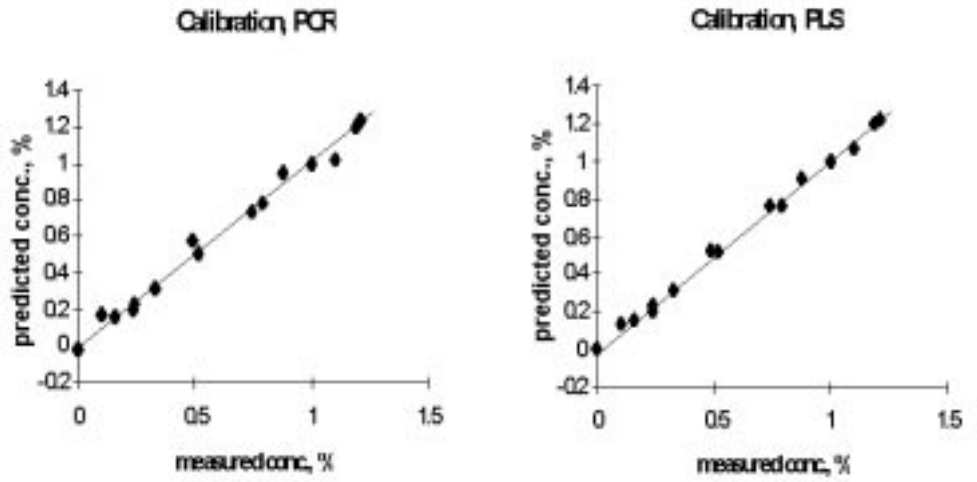

Figure 3. Calibration curve using PCR and PLS models.

Validation

When developing a calibration model, a validation step should be included to evaluate the performance of the model. To test the model, we ran the leave-one-out cross-validation. That is, we removed one sample, and use the rest of the samples to build a calibration model. The model was then used to predict the sample being left out. This step was repeated for each sample. Again the model was based on PCR and PLS methods. The advantage of doing cross-validation is that,

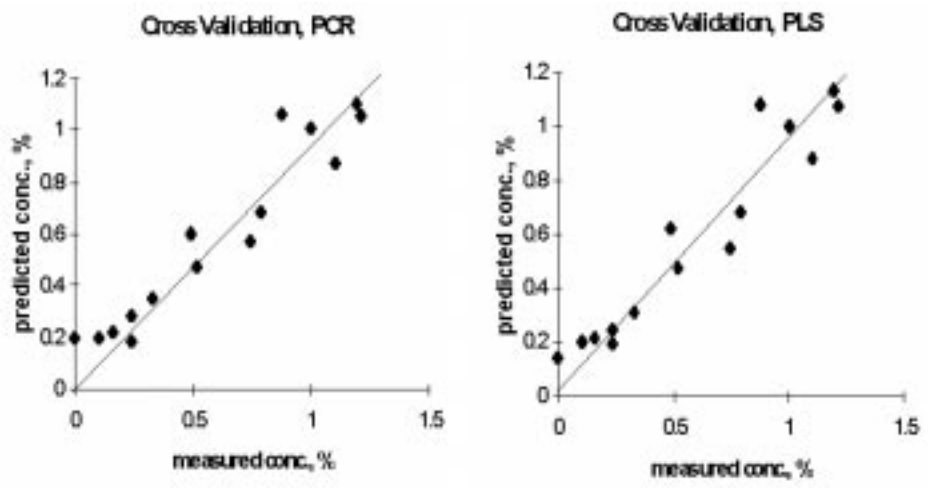

Figure 4. Cross-validation curve using PCR and PLS models.

unlike calibration with a full data set, the sample being predicted is not included in the calibration model. In this way, the model can be tested independently.

Figure 4 shows the result from cross-validation by PCR and PLS. The x-axis is the concentration measured by GC and weighting and the y-axis is the concentration predicted by the PCR and PLS model, which is built without the sample being predicted. From the error analysis, five principal components were chosen in developing the PCR and PLS cross-validation model. The analysis results are shown in Table 1.

Sources of error and suggestion for future work

Limited number of samples

In analysis of tobacco samples, many sources of variation come into play, such as sample particle size, moisture content etc. This complexity requires a higher number of representative samples to be included in the calibration set. A large number of calibration samples is required to ensure that the variation of these unrelated factors is statistically random in relation to the variation of menthol concentration. Usually more than 100 samples should be prepared for development of a calibration model, and approximately another 50 samples for the validation set. Often, a calibration will be developed with a smaller number of samples and the number of calibration samples will be increased over time. Thus, the accuracy of the calibration will improve over time.

Table 1. Results of calibration and cross-validation, including standard error of calibration (*SEC*), standard error of cross-validation (*SEV*) and correlation coefficient (r^2).

Parameter	*SEC*	*SEV*	r^2
PCR (5)	0.10%	0.19%	0.98
PLS (5)	0.03%	0.12%	0.99

Reference methods

The accuracy of concentration information is critical in calibration. It is recommended that more samples be collected for GC analysis in order that we may have a better idea of what is the error in the reference method and how it propagates into the calibration model.

Conclusion

From these preliminary tests, we concluded that a PCR and PLS model give reasonable predictive ability. With more efforts involved in calibration, a model can be established for future prediction of unknown sample concentrations based on their reflectance spectra. Compared to conventional laboratory analysis, NIR reflectance spectroscopy method appears to be a good alternative. The speed and simplicity of this technique is important in a manufacturing plant, where a large number of samples need to be analysed continuously.

References

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