Thermometrical spectroscopy: temperature programming as a control variable to increase information content from near infrared spectroscopic measurements—characterisation of honey samples

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Introduction

Invisible radiation beyond the red end of the visible spectrum was discovered by William Herschel in March 1800.[1] Not surprisingly, Herschel did not understand what he had discovered. He believed that this "heat radiation" was something quite different from light and he suggested the terminology "the thermometrical spectrum" for what we now know as part of the near infrared (NIR) region (which I like to refer to as "the Herschel region", 780–1100 nm[2]) and his suggestion has been long forgotten. In this paper I would like to suggest a new use of this term.

It has been known for a long time that NIR spectra are affected by the temperature of the sample. This is especially true if the sample is present in a liquid form. There have been several studies of the effect of temperature on the spectrum of water[3–5] and Osaki and colleagues have carried out 2D-correlation studies on other liquid systems of organic solvents where temperature is the controlled variable.[6,7] While these experiments have deliberately made measurements at different temperatures, as far as I am aware, the quantitative and qualitative applications of NIR spectroscopy have always seen temperature variation as an interference that has to be managed or avoided. In our work on the characterisation of honey,[8] I deliberately introduced temperature variation. I believed that this would help the discrimination because the expected variation in the sugar composition of the samples would have a varying influence on the spectrum of the water in the sample. The first paper giving the results of the experiment has been accepted for publication in the Journal of Near Infrared Spectroscopy[8] and need not be repeated in detail except to explain how these experiments in "Thermometrical spectroscopy" were performed. Then I will discuss how they might be incorporated in future NIR spectroscopic systems.

Experimental system for honey characterisation

The system used for the characterisation of honey was based on the use of a Foss NIRSystems NIR 6500 spectrometer (Foss NIRSystems, Silver Spring, MD, USA). Honey samples were scanned using a special sample cell prepared for these experiments, which allowed a small sample of honey to be held in a water bath while NIR measurements were made via a fibre optic probe. The cell, was made by cutting out a cell in a solid brass cylinder (60 mm tall by 25 mm diameter) so that a minimum amount of

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sample was lost in covering the bottom 25 mm of the probe whilst allowing the sample to flow into the measuring cavity of the probe. The warm honey sample, 7–10 g, was placed in the cell and the probe was slowly inserted so that honey would flow into the measuring cavity of the probe. The cell was maintained at one of five chosen temperatures (10, 17, 26, 37 and 50°C) by immersion in a thermostatically controlled water bath, Grant 6G (Cambridge, UK). NIR spectra over the range 1100–2498 nm, were recorded at 2 nm intervals. The cavity, between the end of the probe and mirror was set at a gap of 2 mm giving a path length of 4 mm. Three NIR spectra were recorded at each temperature using the empty cell as the reference measurement for the calculation of transmission (T) spectra as $\log(1/T)$. The recorded spectra were transferred to the hard disk of a personal computer.

Data Analysis

The recorded NIR spectra were transferred to the UNSCRAMBLER (Camo AS, Oslo, Norway) environment for graphical plotting and some preliminary mathematical treatment. Selected portions of the spectra were plotted before and after the calculation of second derivatives using a seven point,

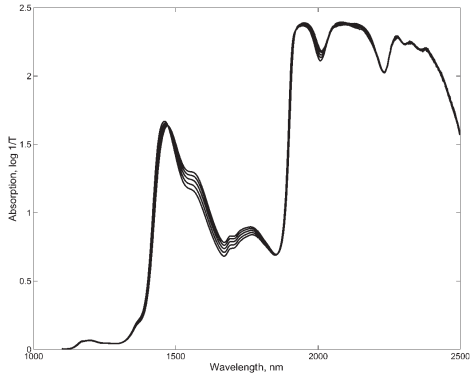

Figure 1. Raw spectra of one honey sample at five temperatures.

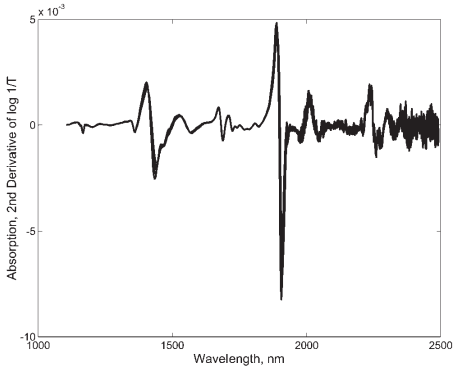

Figure 2. Second Derivative of spectra shown in Figure 1.

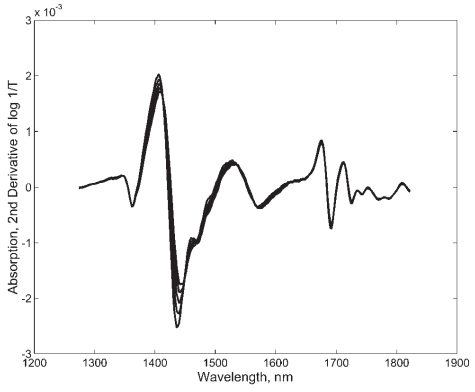

Figure 3. Selected region of second derivative spectra of a honey sample measured at five temperatures.

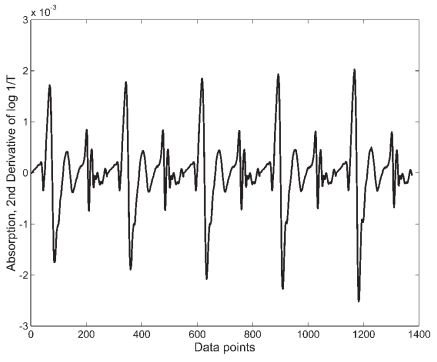

Figure 4. Psuedo spectrum of the selected region of a honey sample measured at five temperatures. The temperature increases from left to right.

second order Savitzky–Golay filter. The data were then transferred to the MATLAB (The MATH WORKS, Natick, MA, USA) environment for subsequent data processing.

The three derivative spectra for each temperature measurement were averaged. For each honey sample, a selected region from 1274 to 1822 nm (275 data points) of each of the averaged derivative spectra for each temperature were combined to make a pseudo spectrum (PS), which combined temperature and NIR measurements of 1375 data points. The processing sequence for a single sample is shown in Figures 1–4. The PSs were then compressed by principal component analysis (PCA) into twenty principal components (PCs).

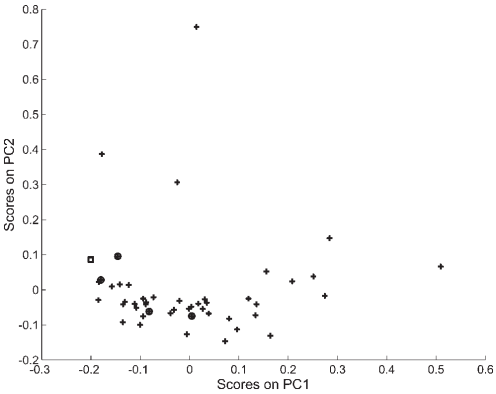

Figure 5. A scores plot of the first two PCs indicating the position of the rape samples (circles). The square symbol indicates the position of a rape sample which was excluded from the PCA.

Canonical variates analysis (CVA) was used to attempt to form groups of honey with five or more members into clusters using 5, 10, 15 or 20 PCs. Cross-validation (leaving out one sample in turn as a test sample, carrying out the calculations on the rest of the samples and then predicting the excluded sample) was used to test each of the 28 members of these groups for membership when they were not used in the computation of the clusters. Figure 5 is a typical scatter plot of the first two PCs for the rapeseed group and Figure 6 is an overview plot of the results of the CVA for the four groups.

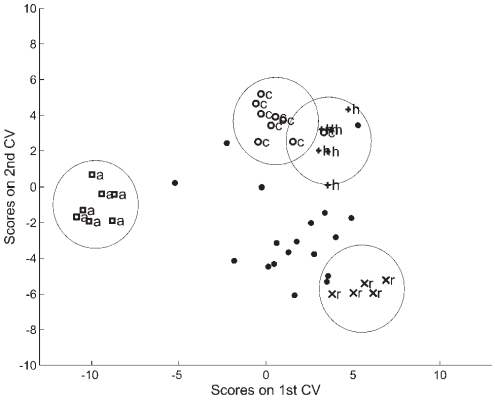

Figure 6. Plot of first two CVs from the CVA of the 28 honeys belonging to one of four groups; a, acacia; c, chestnut; h, heather and r, rape. The unlabelled dots indicate the calculated positions of the twenty honeys which are not members of any of groups in the CVA. The ellipses around the groups are at a confidence level of 0.95.

Discussion

Some preliminary analysis has found evidence that the temperature programming made a contribution to the generally satisfactory results from the honey experiment but this is not required for the discussion of the general idea of introducing deliberate variation in sample temperature. The system used in the honey experiment was very slow to use and impractical for regular application. In the current study it took an average of 45 minutes to make the measurements on one sample, taking three spectra at each of five temperatures. The majority of this time is due to the use of a water bath.

More practical methods are available but the choice depends on the type of spectrometer and the application.

For slow scanning systems (more than one second per scan), the temperature must be at a known stabilised temperature during the scan and this could be achieved by a Peltier effect tem-

perature controlled sample cell. This type of controller can change the controlled temperature much more efficient and would allow measurement of 3 – 4 samples per hour. For fast scanning systems, pulsed heating produced by electrical or by microwaves would be feasible, assuming that the sample is below the minimum temperature of interest.

Application

Slow scan system

- Spectra at a few (5–20) known temperatures
- Gives Added information
  - Improved qualitative analysis
  - Improved quantitative analysis?
  - Search required for most useful temperatures?
  - CARNAC[9]

Rapid scanning system

- Spectra at many temperatures
- New techniques become possible
  - Develop a temperature calibration and an analyte calibration at a given temperature
  - Use the temperature calibration to find the spectrum of the required temperature
  - Use that spectrum to estimate analyte

While thermometrical spectra from slow scanning systems might give some useful information, the possibilities for fast scanning systems are much more interesting. The idea is that during the calibration phase calibrations for the analyte at a given temperature and a temperature calibration would be produced. In use, the thermometrical spectra would be searched to find the spectrum closest to the calibration temperature and this spectrum would be used to predict the analyte concentration of the sample. It would have application wherever sample temperatures cannot be easily control. Biomedical measurements would be an especially interesting application as patient body temperature can introduce serious errors.

It could be said that thermometrical spectroscopy has been dormant for 200 years. In order to end this dormant phase, instrumentation and funding are required for the idea to germinate.

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