Examining the components of ground paprika

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Introduction

Paprika spice(red pepper) is commercially cultivated in Hungary. Its various products, such as powder, paste and oleoresin, are excellent food colourants. However, it is still a serious problem for paprika producers and consumers that ground products lose their colour during a relatively short storage period. It has been shown that a radical shift in the colour of the product, even though accompanied by no change in flavour, can make it completely unacceptable. Several analytical studies focus on the carotenoid ester composition of paprika fruits.[1–3] The results showed that fatty acid esters of capsanthin and capsorubin are the major constituents of paprika pigment.

In Hungary paprika spice has been subjected to quality control for over 78 years. From the very beginning there was the visual inspection of colour (colour test), but once developed a method[4] for the determination of pigment content, visual inspection of the colour became the second parameter of grading. The Hungarian Standard[5] for the first time specified paprika spice according to the pigment content. Several authors applied colorimetric and spectrophotometric methods in the testing of paprika.[6–8] However, colorimetry could not give detailed information on the compositional changes in red pepper as a function of processing and storage. The effect of some varietal and technological factors on the content and composition of colour and pigment and other vital bioactive materials in paprika spice has been the subject of many recent investigations.[9] Technological factors most likely to effect the quality of paprika may include overripening, drying (time and temperature), milling (type, temperature and powder fineness) and storage conditions.

So the objectives of the investigations were to study the colour change during storage, the effect

Table 1. The list of all varieties of paprika involved in the investigations

Name	Sweet	Hot
62-80	√	
Fo3csip		√
Csardas	√	
Km-622-50	√	
Cseresznye		√
K-90		√
801	√	
Km622-lev	√	
K178-lev		√
K178-csip		√
K178-90		√
Csipos-70		√
Sz-20	√	
622-90	√	
Km622-70	√	
K178-50		√

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of drying and that of variety on paprika spice using near infrared (NIR) spectrometry, colorimetry and HPLC analyses.

Materials and methods

The fruits of different cultivars of paprika spice (*Capsicum annuum L.*) were obtained from the Research Station for Paprika Development (Kalocsa, Hungary). Paprika fruits, whose names and characteristics are displayed in Table 1, were hand-picked in the first half of October, 1998. At that time the weather was chilly and rainy. After that all cultivars were subjected to after-ripening for a period of three weeks under ambient conditions. Also, some 20% of the initial water content was removed during this time. They were then cut into smaller pieces and dried by a forced-air technique using an experimental cabinet drier (Labor MIM, Hungary) with variable air temperature (50, 70, 90 centigrade) for ten hours. The airflow was at a superficial velocity of 2 m s^{-1}. Half a kilogram of each cultivar was dried by this method. For the following analyses, dried paprika was ground by a coffee mill and passed through a 0.5 mm mesh sieve.

Extraction method

Lipid fractions, including carotenoids, were extracted according to a previously described method using methanol to remove water that was reabsorbed. The pigments were then extracted by a mixture of 1 : 1 CCl_4-chloroform containing methanol up to 20%. A mixture of 2 : 1 : 1 chloroform-acetone-isopropanol was applied to extract lipid fractions from ground paprika samples. 0.5 g of every sample was taken and 50 ml of the above mentioned mixture was added to it. Then the samples were shaken, filtered and distilled (Rotadest) at 35ºC. 10 mL was then used for HPLC analysis.

HPLC determination

A Beckman Liquid chromatograph was used, consisting of a Model 114 M isocratic pump, a Model 165 variable wavelength UV-visual detector and a Model 340 organiser equipped with a 20 µl loop injector. The signal was electronically integrated by a Shimadzu C-R3A or Waters-740 Data Module integrator. All measurements are the average of two replicates.

NIR analysis

The samples for the NIR analysis were taken from the ground (coffee mill) paprika. They were then loaded into standard rotateable cuvettes. The samples were measured on a weekly bases in order to try to follow, if possible, the change in the amount of colour substances. So that is why the samples were kept in the cuvettes with the glass facing down. This prevented the light from catalysing colour degradation. The cuvettes, if sealed and loaded in a proper manner, can be considered as almost airtight.

Diffuse reflectance spectra were recorded in the 1100 to 2500 nm range with 2 nm increments using a Foss NIRSystems 6250 (Silver Spring, MD, USA) grating monochromator equipped with PbS detectors.

Each spectrum was recorded as the average of 32 scans. All cuvettes were rotated twice at 120º angles to try and minimise the affect of sample inhomogeniety. Thus, three spectra were averaged to represent a sample. The log1/R spectra were smoothed and 2OFD (second order of finite fifference) function was applied to correct for baseline shifts and to resolve overlapping absorption bands. Then principal component analysis (PCA) was performed on a centred data set to decompose the spectral information onto a few orthogonal variables. Visual inspection of the pretreated spectra and those of the loading spectra helped to get information for selecting wavelength ranges and to develop teaching models. Based on those individually optimised PCA models, a SIMCA algorithm was used for classi-

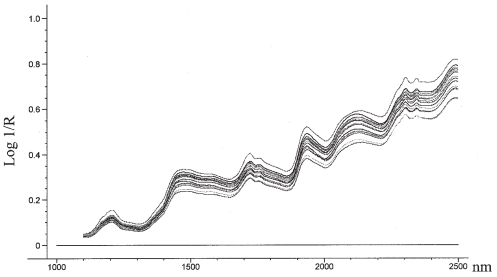

Figure 1. Raw spectra (log 1/*R*) of all varieties of paprika after the first measurement.

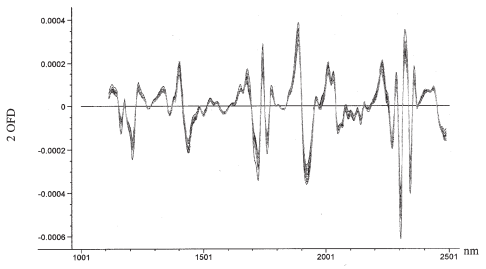

Figure 2. Second derivative (2 OFD) spectra of all varieties of paprika after the first measurement.

fication. The pretreatments and all calculations were carried out using Unscrambler 6.1 (CAMO, Trondheim, Norway) for Windows 95.

Colour measurement

Samples were measured using the Momcolor-D tristimulous colorimeter as well. This device has a 25 W lamp, four colour filters, selenium detector, a low resistance preamplifier and digital voltammeter, display and a stabilised power source. The samples were measured in the visual range in the same cuvettes as in case of NIR. As a reference material the white standard was used, so all values are interpreted relative to that. The samples were measured on a weekly basis and three recordings of every sample were averaged to improve accuracy. After obtaining *X1*, *X2*, *Y* and *Z* values, they were transformed into a^*, b^* and L^* values. These values were then further processed to give chroma difference, hue difference and lightness difference, the sum of which is the overall colour difference between the samples. The formulae describing the transformations are beyond the scope of this article.

Results

As the first step for NIR analyses, the raw spectra of all samples were recorded. These spectra are displayed in Figure 1. As it well known, raw spectra are not so informative due to overlapping absorption bands. So these spectra were then transformed into their second derivatives to get a higher resolution of absorption bands and to eliminate the baseline shift.

These spectra are shown in Figure 2. All second derivative spectra were calculated using the Savitsky–Golay algorithm. This formula fits an *n* order polinom to the spectrum in question. Upon visual inspection of many different combinations of polynomial order, number of left and right side points and the degree of derivation I found that a second order polynominal with second derivative and 6–6 left and right side points is the best trade-off between resolution enhancement and low noise. On this graph it is clear that the water and oil peaks are abundant. All further processes were carried out using second derivatives with these parameters.

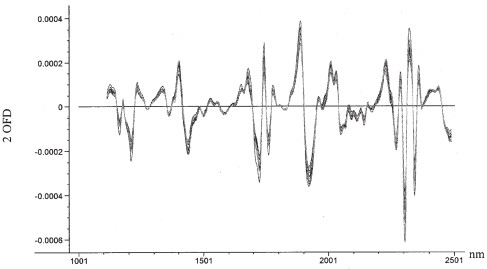

Figure 3. PCA score plot of all varieties of paprika in the space of the first two principal components. The whole spectral range was used.

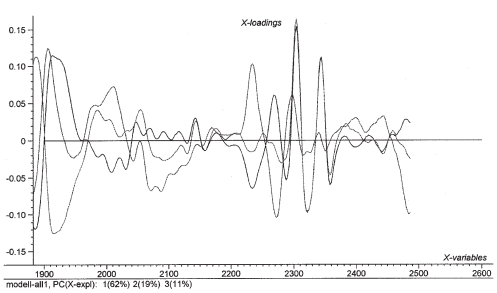

Figure 4. Loading spectra of the first three principal components.

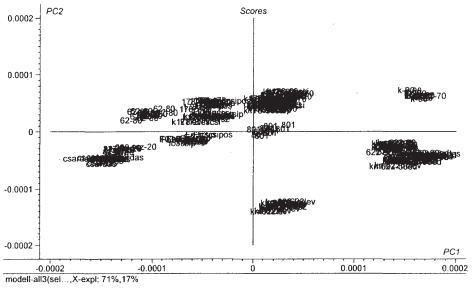

Figure 5.PCA score plot of all varieties in the space defined by the first two principal components. The selected wavelength ranges were used.

To explore whether there is a structure or pattern in the data set, a PCA was performed with all variables and all samples. This is illustrated in Figure 3. This two-dimensional score plot reveals that the csceresznye variety is a potential outlier and wavelength selection is needed to achieve a better separation. This is reinforced, to some extent, by the influence plot, which is a combination of the leverage and the residual calibration variance. Cseresznye, by the way, is a "hot" variety. The so-called data reduction was done by using six PCs and the whole spectral range. As a means of validation full cross-validation was applied. Then the analysis of the loading spectra, which can be seen in Figure 4 and those of the second derivative spectra, led to the selection of certain spectral ranges. These ranges are as follows: 1980–2006 nm, 2200–2244 nm, 2294–2314 nm, 2334–2352 nm. Then another PCA was performed with the selected wavelength ranges and the score plot of this is displayed in Figure 5. Based on the results of this PCA, SIMCA analysis was performed, the plot of which is seen in Figure 6, which shows the varieties in the space of two PCA teaching models, one for all sweet varieties and one for all hot varieties excluding csceresznye. It is clear that the sweet and hot varieties can be separated and there are some other groups as well.

This gave me the idea that, perhaps, *KM* sweet varieties and the *K-178* hot varieties can be taken for SIMCA classification. But before doing this new wavelength regions were selected, which are as fol-

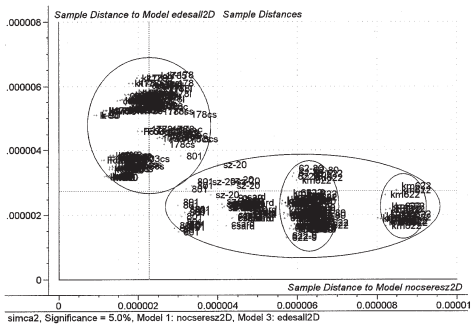

Figure 6. Cooman's plot of the sweet and hote varieties as defined by two PCA models, one for all sweet varieties and one for all hot except the csceresznye varieties.

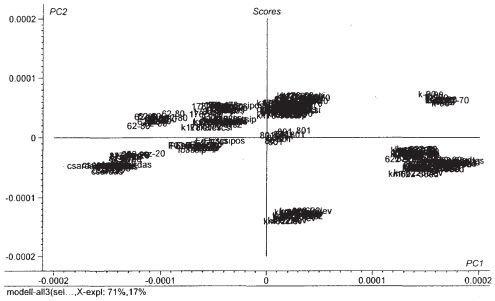

Figure 7. Cooman's plot for displaying the difference between the drying conditions of the *KM* varieties.

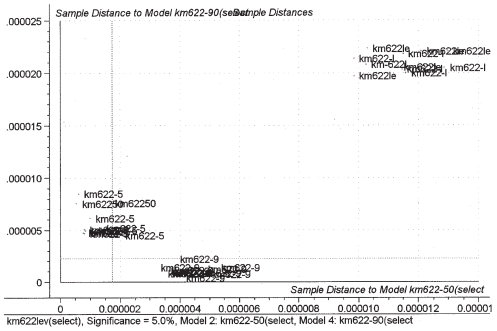

Figure 8. Cooman's plot for displaying the difference between the drying conditions of the *K-178* varieties.

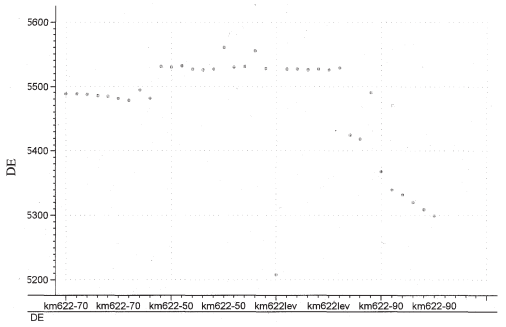

Figure 9. The colour difference plot of the *KM* varieties based on colorimetric data. The number on the vertical axis have not units, they are only a measurure of the difference relative to a standard.

lows; 2246–2254 nm, 2292–2314 nm, 2336–2352 nm. As there are four different drying temperatures four different individual PCA models were created and optimised. These PCA models served as the basis for the classification. The results can be seen in Figures 7 and 8. The former differentiates between *KM* varieties treated under ambient temperature, 70ºC and 90ºC, respectively. The uppermost group is the air-treated one (ambient and air-treated are used with the same meaning here), while the second group is the one dried at 70ºC and the last one is the 90°C group. This means that classification with SIMCA, using the selected wavelength ranges, is good for distinguishing the varieties treated under different temperatures.

The next plot is for the *K-178* varieties in the space of the 90°C and the air-dried group.

The same statements apply for this plot as for the previous one, except that the middle group is the 50°C group.

I also tried to find some link to storage time, the degradation of different substances and the NIR spectra, but the results were so confusing that I considered it unsuitable for interpretation.

I also examined all varieties with colorimetry in the same manner as in case of NIR, but only the different drying temperature plots are in accordance with the NIR results, i.e the colour difference *DE** correlate to the SIMCA plots of the corresponding *KM* and *K-178* varieties. The chart for the *KM* varieties is shown in Figure 9.

This figure shows the so-called colour difference of the *KM* varieties. The first group is the 70°C group, the second involves the 50°C and the air-dried groups with one outlier due to some type of error and the third is the 90°C group. The same is true for the *K-178* varieties, but in case of the 90°C there is no downward tendency. This reinforces the results of NIR analyses as far as these two varieties and temperature areconcerned. But, as mentioned in the literature, colorimetry is the best method to assess the changes in paprika spice and this was found to be true because the storage time and the sweet–hot results were even poorer than those of the NIR measurements. Thus they are not mentioned here.

Conclusions

The first selected wavelength regions are suitable for separating the sweet and hot varieties from each other, which I think could mean that they have different fat contents and perhaps different amounts of colouring substances associated with them. Second, the effect of temperature could be monitored and the results be used to decide whether the paprika has received the necessary treatment or perhaps was over-treated. So these models, with further enhancements, may be useful in at-line,

off-line or on-line measurements. Third, the differences between the sweet and hot varieties are not marked by the degree of temperature applied. Fourth, the changes in the 12-week storage period could not be unambiguously followed by NIR at this stage. Finally, colorimetry could not produce the same results as NIR.

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