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Off-line detection of milling processes of Pannon wheat classes by near infrared spectroscopic methods

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RESEARCH ARTICLE

Abstract

The innovations of near infrared (NIR) technology are effectively used in the quality control field of cereal science and technology. The aim of this study was to elaborate NIR methods for testing and recognition of chemical components and quality in 'Pannon wheat' milling fractions as well as to develop spectroscopic methods following the milling processes and evaluate the milling actions, the stability of the milling technology by different types of milling products. Milling fractions of the 'Pannon Standard' and the 'Pannon Premium' wheat categories were produced from allied (i.e. true to variety or variety identical) wheat under industrial conditions where samples were collected versus sampling times and maximum or minimum yields. The changes of the main chemical components (starch, protein, lipid) and physical properties of fractions were analysed by dispersive spectrophotometers using visible and/or NIR regions of the electromagnetic radiation. Close correlations were obtained between the data of spectroscopic measurement techniques processed by various chemometric methods (principal component analysis, cluster analysis) and operation condition of wheat milling technology. During this task, it became obvious that the NIR methods are able to detect the differences of the maximum and minimum yield settings within one fraction and differences arising from the sampling times by some variety of fractions, respectively.

Keywords: allied wheat categories, milling process, NIR, PCA, CA

1. Introduction

The average composition of a wheat grain is 71.9% starch, 12.2% protein, 1.9% non-starchy carbohydrate and 1.7% ash (Lásztity, 1999). Common wheat (*Triticum aestivum*) is generally classified as winter and spring wheat in the United States and in Australia based on geographical classification (Dexter *et al.*, 2006; Federal Grain Inspection Service, 2013; WQA, 2011). In Europe and also in Hungary diverse specification systems exist, that are based primarily on wheat quality parameters.

The 'Pannon wheat', which constituted the samples during our study, is a certification mark (i.e. one that gives legal assurance regarding the quality or other characteristics of certain products) that certifies the homogeneity and the excellent baking characteristics of the product and gives warranty that it has been produced under controlled conditions (Centre for Agricultural Research, 2011; Parliament of Hungary, 1997). The Pannon Wheat Programme is a complex, regional, export-oriented research and development system involving quality research. The system of Pannon wheat quality criterion was elaborated based on international quality control systems, the technological quality of Hungarian wheat varieties, and the cultivation conditions in Hungary. The Pannon wheat is comprised in two kind of categories, one of the Premium categories which are hard-grained, milling quality, high wet gluten content, and excellent dough quality. The other category is the Pannon Standard the criterion of this category is less strict than the Premium category (Centre for Agricultural Research, 2011).

Industries involved with foods and beverages have traditionally used near infrared (NIR) spectroscopic measurements for quality control, blending, and process control and made it possible to directly measure not only the physical characteristics (e.g. hardness and particle size) of the kernels but also different chemical constituents of the grain products (Huang *et al.*, 2008; Workman *et al.*, 1999). During the innovation of food and biotechnological processes an important task is to produce high biological value products, rich in bioactive and health promoting components having special functional properties. To achieve this, one of the key priorities is in the improvement of the analytical and extraction methods that are fast enough and able to detect bioactive components both qualitatively and quantitatively and eligible to be used for online monitoring and to be integrated into the process analytical technology (PAT) system (Salgó *et al.*, 2009). The development of the on-line NIR technique allows real-time monitoring. Online NIR devices allow the detection and improvement of grain and cereal product quality from on all levels ranging the raw materials (i.e. grain and flour) to finished goods (i.e. bread, extrudates, etc.) (Evans *et al.*, 1999; Pojić *et al.*, 2012; Vigni *et al.*, 2009).

So NIR spectroscopy as PAT tool (Van den Berg *et al.*, 2013) has been integrated into monitoring the milling process, which is an important system of controlling technologies in terms of quality, stability and yields of the final product. The literature reports several examples of examining flour mixtures, but these prefer to observe one kind of bakery products or raw materials, in contrast to our study monitoring different fractions of flour, which were carried out simultaneously to highlight the difference between the products during the milling process and to monitor the separation technology. The main aim of this study was to monitor the chemical and physical characteristics of milling fractions by the NIR technique in industrial environment, measuring the variability of the different kinds of products according to the sampling times and different technology settings, respectively.

2. Materials and methods

Samples

The *T. aestivum* wheat origin milling fractions were produced by Gyermelyi Corp. flour-mill and pasta factory (Gyermely, Hungary). Two mills are existed in the area of factory, one is capable to grind 300 t wheat per day; the other has a capacity of 200 t per day. Our examined milling fractions were produced by these two mills. The applied technology is originated from Bühler AG, Uzwil, Switzerland, and it is their patent. The same silo was used during all feeding trials using so-called closed system milling process, and allied wheat sharing genetic and environmental background were separated allowing the use of wheat flour of identical quality during all experiments.

The samples were examined from two aspects during the measurements. In the first trial, allied wheat milling fractions (i.e. (42×3 samples) 'Pannon Standard' fractions) in compliance with Codex Alimentarius Hungaricus (WF55, WF80, WF112, FP50 where 'WF' and 'FP' mean 'wheat flour' and 'flour for pasta', respectively, and the number after abbreviation refer to the ash content in hundredth of %) (Ministry of Agriculture and Rural Development, 2007) were produced under industrial conditions where samples were collected various sampling times at 8 am, 12 am, 4 pm, 8 pm, midnight and 4 am on the following day. And used an aleurone-rich flour (ARF) which is a newly-developed experimental wheat flour (Table 1.), was also produced and developed at Gyermelyi Corp. with the cooperation of the Department of Applied Biotechnology and Food Science, Budapest University of Technology and Economics, Budapest, Hungary and Bühler AG (Bagdi *et al.*, 2014).

The advantage of collecting samples in different times to follow the stability of milling technology. Hereby getting more information about the quality changes of the flour fractions. The main demands of customers and of course the owner of the mill factory to produce same quality milling

Table 1. Ingredients of the aleurone-rich and endosperm-rich milling products (Bagdi *et al.*, 2014; Lásztity, 1999).

Ingredients	Aleurone-rich flour (g/100 g)	Endosperm-rich products (standard fractions) (% dry weight basis)	Wheat flour WF112 (% dry weight basis)
Moisture	–	10.4	11.04
Ash	3.83	1.7	0.91
Protein	26.67	12.2	19.12
Starch	47.65	71.9	67.25
Total dietary fibre	17.59	1.9	–
Total fat	–	1.9	–
Crude fat	4.26	–	1.68

finished goods. From milling perspective, the differences between FP and WF are mainly realised the particle size and amount of bran content, respectively. The WF fraction has smaller particle size (e.g. most part of it under 250 µm; 95%), than FP fraction (e.g. most part of it between 200 and 400 µm; 85%) (Ministry of Agriculture and Rural Development, 2007).

The ARF fraction was investigated during a 24 hour experiment, the sampling times were equal (8 am, 12 am, 4 pm, 8 pm, midnight and 4 am on the following day) than by the standard fractions. During the second trial allied wheat belong to the 'Pannon Premium' category (i.e. Saturnus (30×3 samples)) and compliant to Hungarian standards (WF55, WF80, WF112, FP50) as well as ARF were used. During this second experiment 24 hours of the day were partitioned. The first half of the day was dedicated to getting the maximum yield of the FP ('flour for pasta') fraction, so sampling times were at 7 am, 10 am and 1 pm. The second half of the day was aimed at getting the minimum yield of the FP fraction, so sampling times were at 3 pm, 6 pm and 9 pm. The 5 fractions along with the FP were also examined during each approach. The FP yield settings were changed according to the customer claims of the flour-mill and the pasta factory, if the pasta factory has to be produced more pasta products the flour-mill is operating higher FP yield setting, otherwise the minimum FP yield setting is used. The minimum FP yield is approximately 22% and the maximum FP yield is 32%, respectively.

Reference materials

The reference materials originated from Sigma Chemical Co. (St Louis, MO, USA). There were gluten from wheat, unmodified wheat starch and wheat germ oil. The confirmatory measurements were realised according to international standards (AACC, 1999).

Spectroscopic measurements

Samples and reference materials were scanned using dispersive instrument to collecting the raw spectra. Three independent scans (i.e. three scans were recorded for each sample and the means of these replicates was used in subsequent calculations) were recorded from each spectral sample. The dispersive NIR instrument, NIR Systems 6500 monochromator system (Foss-NIR Systems, Silver Spring, MD, USA) fitted with a rapid content analyser and micro-sample cup equipped with threaded back. Samples were scanned from 400 nm to 2,498 nm in reflectance mode (R mode: Si detector, 400-1,098 nm; and PbS detector, 1,100-2,498 nm). Data were collected every 2 nm (1,050 data points per spectrum).

Data processing

Spectral and reference data were processed using Vision 3.20 (Minneapolis, MN, USA), Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA, USA), Statistica 11 (StatSoft, Inc., Tulsa, OK, USA) software packages. Used the second order derivatives (D2OD) 8/0 nm gap-segment (Hopkins, 2001; Norris, 1983) setting in the case of each spectra and after with these derivatives spectra were applied principal component analysis (PCA) method (Martens and Naes, 1991; Wold *et al.*, 1987) and cluster analysis (CA) method (Heise and Winzen, 2002), respectively.

3. Results

The separation of the raw spectra of the 5 fractions (WFs, FP and ARF) during the first trial and the differences of the raw spectra of the reference materials are shown in the measured wavelength range (Figure 1A and 1B, respectively). The huge baseline shift between the FP50, ARF and the WF fractions are caused by two factors: the deviation of the ARF and FP50 fractions from the WF fractions derive from the difference between chemical and physical properties. In the case of ARF colour causes the main variability in the visible range (400-800 nm in Figure 1A), because it has a higher aleurone amount than the WF fractions, while the FP50 fraction represents a bigger average particle size (i.e. particle size is 400 µm in the case of FP50 fraction and 315 µm by WF fractions) (Ministry of Agriculture and Rural Development, 2007).

The second order derivatives of the NIR spectra (D2OD) were calculated using all types of samples to check the absorption bands for more details. The D2OD 8/0 nm gap-segment setting was used to retain sensitivity and give more separable gaps of milling fractions than other gap-segment settings. The 1,700-1,800 nm wavelength is highlighted based on the sharp distinct of milling fractions (Figure 1C). The D2OD 8/0 nm spectra of the main components (i.e. starch, protein and lipid) also have (Figure 1D) characteristic peaks closer to each other, which influences the shift of sample spectra. Comparing the D2OD 8/0 nm spectra of the samples (Figure 1C) to the reference materials (Figure 1D) in the range 1,700-1,800 nm, high variability of all main components is detectable. The D2OD 8/0 nm spectra of WF55, WF80, WF112 and FP50 fractions peak at 1,748 and 1,780 nm (Figure 1C), which represents starch (Figure 1D). The special test-fraction, ARF has absorption bands around 1,725 and 1,760 nm (Figure 1C) owing to protein and lipid, and lipid respectively (Figure 1D). Therefore, the difference between the WFs or the FP50 (mainly starch) and the ARF fraction (mainly lipid and protein) becomes prominent as far as assignation is concerned. In the study of Miralbés (2003) the main components of wheat were examined in the case of the different types of wheat categories and different yielding area (i.e. France, Spain) by NIR method (i.e. hard

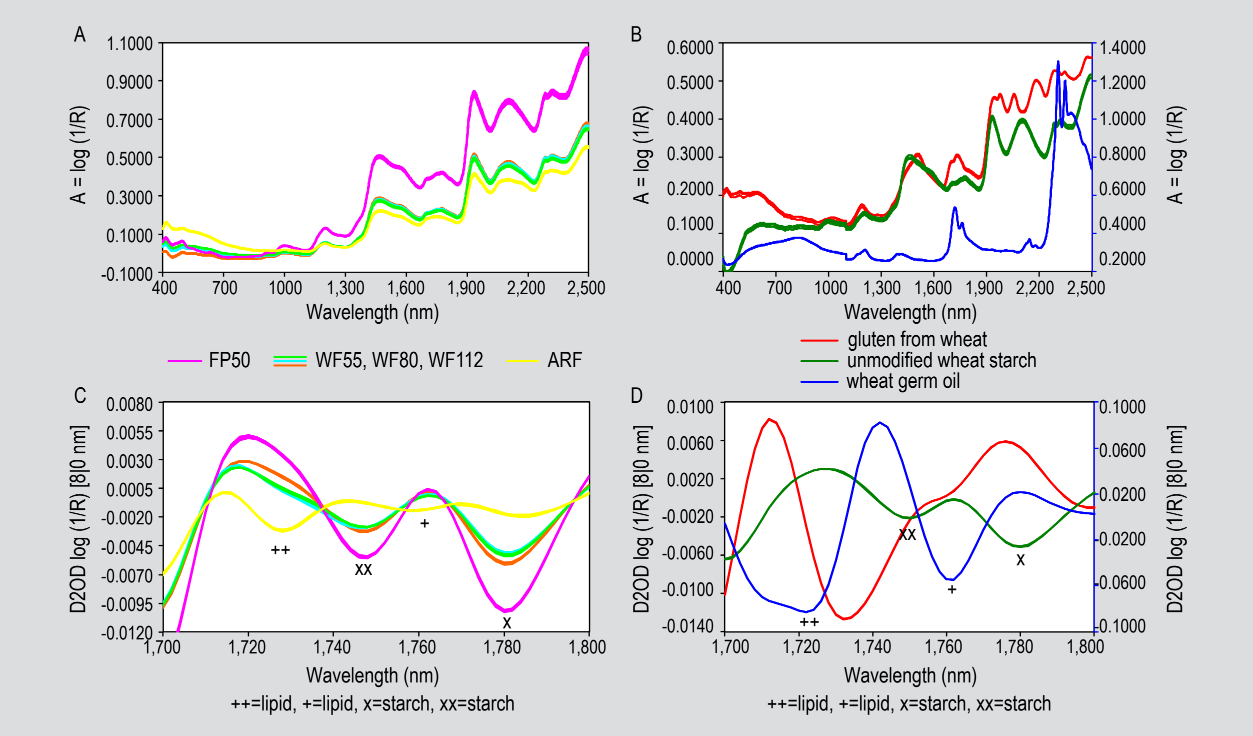

Figure 1. Visible/near infrared (NIR) spectra of the (A) wheat fractions (WF = wheat flour; numbers refer to % ash content; FP = flour for pasta; ARF = aleurone-rich flour) and (B) reference materials in the wavelength range (400-2,500 nm), and second order derivatives of the NIR spectra (D2OD 8/0 nm) in the priority range (1,700-1,800 nm) of the (C) fractions and (D) reference materials during the first trial.

and soft wheat) and the NIR was able to distinguish between these samples. In the above-mentioned reference study, the wheat fractions were not originated from the same field or from the same silo, hereby the separations of different types of wheat categories were more obvious by NIR. On the other hand, in our study the examinations with NIR are realised in the case of the allied wheat (i.e. 300 t variety identical wheat flour) from the same categories, from the same type of wheat, from the same silo. Hereby can survey the distinguish of the allied wheat factions.

In the first trial of milling fractions using 'Pannon Standard' wheat (Centre for Agricultural Research, 2011), different groups according to sampling time at the 1,730-1,765 nm wavelength range had been created. The D2OD 8/0 nm spectra of two kinds of fractions were separated well according to the sampling time (i.e. 8 am, 12 am, 4 pm, 8 pm, midnight and 4 am on the following day) the WF112 standard half-white flour product with higher bran amount (Figure 2A) and the ARF product (Figure 2B). Checking the D2OD 8/0 nm spectra of the other three fractions (i.e. WF55, WF80, WF112) shows no visible deviation according to the sampling times (data not shown).

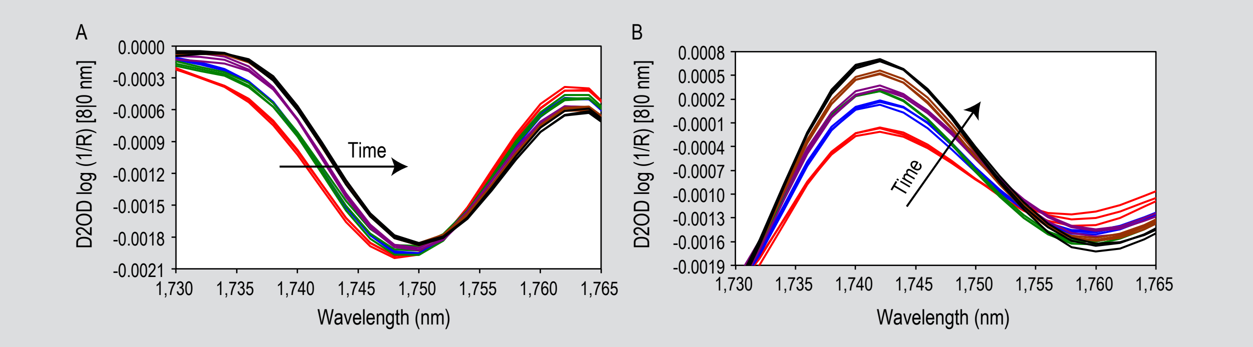

Figure 2. The second order derivatives of the near infrared spectra (D2OD 8/0 nm) of (A) the WF112 and (B) the aleurone-rich flour fractions during the first trial, priority range (1,730-1,765 nm) follow the time goes by.

The question is, why the ARF and the WF112 fractions had more sensitivity peaks of the main components than the WF55, WF80 and FP50 fractions in the range of 1,700-1,800 nm reflecting the changes by sampling times. The scores of the 2nd principal component form distinct groups in the case of the WF112 and the ARF fractions. In the case of these two kinds of fractions, there are principal differences in the composition of the WF112 and ARF fractions, as far as ash, moisture, starch, protein and total dietary fibre contents are concerned (Table 1.). To highlight the difference between sampling times we used PCA in the 1,100-2,498 nm wavelength range of the D2OD 8/0 nm spectra during the first trial (Figure 3).

The huge deviations of the samples based on the sampling times are shown in Figure 3 in the case of the ARF and the WF112 fractions, which yields a visible decreasing trend. The Pearson correlation values (*r*) were calculated between the D2OD 8/0 nm spectra of the reference materials and the first two loadings of PCA (i.e. correlation of protein, starch and lipid in the case of the WF112 and the ARF fractions during the first trial, correlations are significant at $P<0.05$). Checking the correlation in the case of the WF112 and ARF fractions, the loadings of PC2 correlate with protein ($r=0.4722$), and with protein ($r=0.3557$) and lipid ($r=0.3292$), respectively. The ARF fraction has a higher lipid and protein content, than the endosperm-rich WF112 fraction (Table 1), so the correlation value of loadings for PC2 vs D2OD 8/0 nm spectra of lipid in the case of the ARF fraction is increased. The high correlation between the loading of PC1 and D2OD 8/0 nm spectra of starch shows the starchy wheat seed origin, in the case of the WF112 ($r=0.9779$) and ARF ($r=0.9449$).

In the second trial milling 'Pannon Premium' wheat (Centre for Agricultural Research, 2011) the main aim was to evaluate the influence of the settings of the maximum and minimum yields of the FP in the case of the fractions. The settings of maximum and the minimum yield are important for the aspect of the demands of the market. The definition of the yield is, how many flour could be produced from defined wheat amount. The yield is a flour-mill industry value, and is adapted to the directive of the given technology. The main aim of the changes of the yield settings is to produce defined quality products according to the claims of the market. Comparing the maximum and minimum yields of the FP with PCA methods by all fractions, in the case of the WF112 and ARF fractions, a systematic separation of scores of PC1 and PC2 was observed (Figure 4). Checking the PCA score plots in the case of the WF112 fraction (Figure 4A and 4B) during the first half of the day the maximum yield of FP at 7 am, 10 am and 1 pm, and during the second half of the day the minimum yield of FP at 3 pm, 6 pm and 9 pm separate well with score values grouped by the yield of the FP. So sharp deviation could be observed between the two kinds of settings. By the correlation of the WF112, the loading of PC1 (Figure 4A) correlates with starch ($r=0.9759$) and the loading of PC2 (Figure 4B) with protein ($r=0.4628$). So according to the PC1 and PC2, the change of the setting influences the starch and protein ratio, respectively. The WF112 fraction has more starch content in spite of this the ARF fraction has more lipid, protein content, if checking the main chemical components. In the case of the ARF fraction by the loading of PC1, there is no so sharp separation in relation to the sampling time, compared to the WF112 fraction. The reason is that the loading of PC1 of the ARF fraction (Figure 4C) correlates with starch ($r=0.9362$) and protein ($r=0.7621$) too, the correlation of the starch is reduced and in contrast the protein is increased compared to the WF112 fraction. The loading of PC2 of the ARF fraction (Figure 4D correlates with lipid ($r=0.5442$), which is a very good correlation value as far as the influence of the PC2 is concerned and it is clearly reflected in the trend by the sampling times. So these two fractions are very sensitive for the chemical content changes. During the second trial, the minimum yield of the FP results are reduced starch content (i.e. FP50 fraction have high starch content, endosperm-rich product;

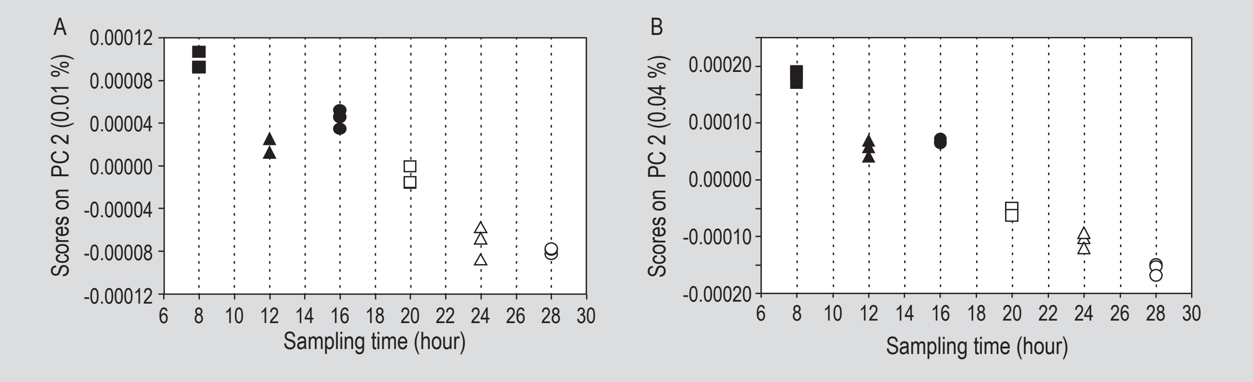

Figure 3. The 2nd principal component (PC2) vs sampling times score plot based on the second order derivatives (D2OD 8/0 nm spectra) of (A) the WF112 and (B) the aleurone-rich flour fractions during the first trial, follow the time goes by.
Sampling time: ■8 = 8 am, ▲ 12 = 12 am, ●16 = 4 pm, □20 = 8 pm, △24 = midnight, ○28 = 4 am on the following day.

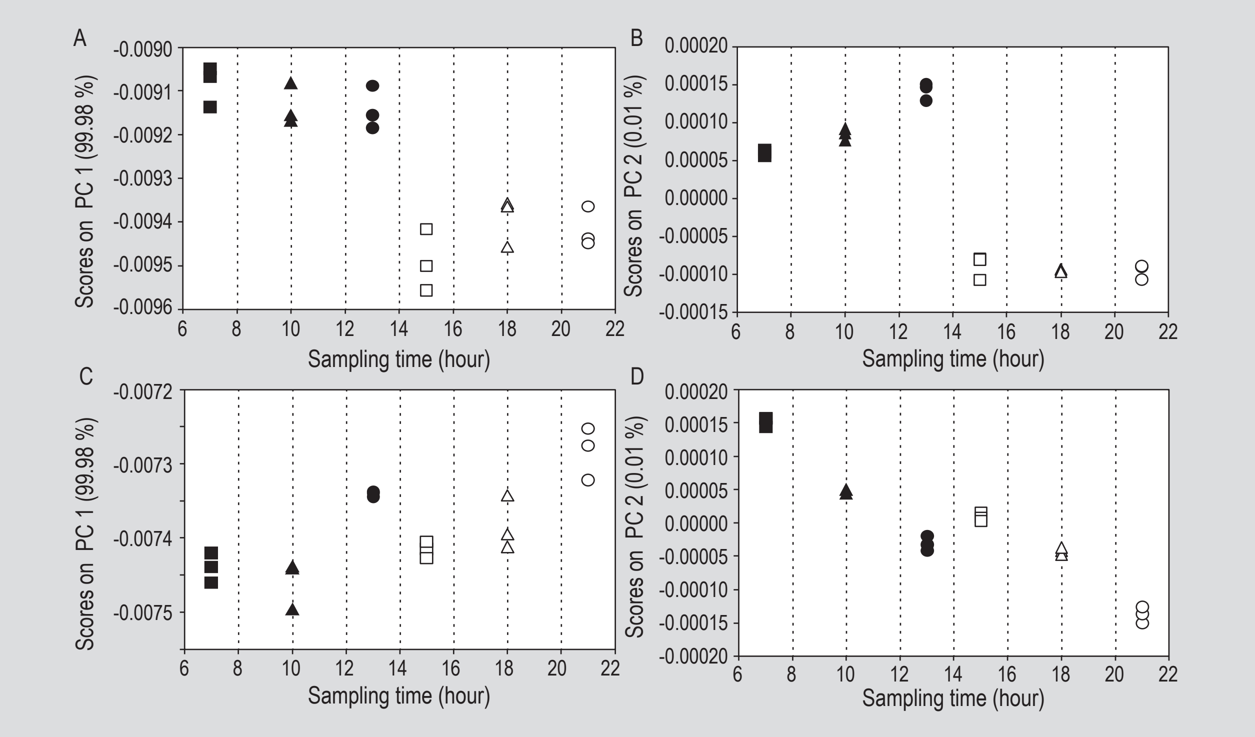

Figure 4. The PCA score plot of (A-B) the WF112 fraction, and (C-D) aleurone-rich flour fraction, (A-C) PC1 and (B-D) PC2 vs sampling times during the second trial based on the second order derivatives (D2OD) 8/0 nm spectra (WF = wheat flour; FP = flour for pasta). Sampling time: ■7 = 7 am, ▲ 10 = 10 am, ●13 = 1 pm maximum yield of the FP, □15 = 3 pm, △18 = 6 pm, ○21 = 9 pm minimum yield of the FP.

Table 1.) and the maximum setting increased it, similarly to the first trial.

Checking the CA dendrogram (Figure 5), wheat fractions separate. The ARF fraction separates first to allow the determination of its different chemical content (Table 1.) such as higher lipid values compared to other fractions. Next, the FP50 fraction separates, which as a larger particle size compared to other standard WF fractions. Finally the three WF fractions separate from each other. The ingredients of the WF fractions are very similar, especially as far as WF55 and WF80 are concerned.

4. Discussion and conclusions

During the evaluation of the milling fractions, not only the difference between the fractions, were examined, but also their stability in quality over time. The differences of the products were represented on PCA score plots and a CA dendrogram after each trial and the ARF, the FP50 fraction in the case of all trials separated well from the rest of the WF fractions. In the case of the ARF fraction, the colour caused major variability (besides the obvious difference in composition), because it has higher aleurone amount than the WF fractions. While in the case of the FP50 fraction, the particle size caused the main variability. The second derivative spectra (D2OD 8/0 nm) peak of the WF55, WF80, WF112 and FP50 are equal with starch peaks, as compared with the reference material spectra. The peaks of the special test-fractions are in compliance with protein and lipid, respectively.

Comparing the maximum and minimum yields of the FP with PCA methods by all fractions, in the case of the WF112 and ARF fractions, a systematic separation of scores of PC1 and PC2 was observed. These settings are influenced the separation of the fractions. During this task, it became apparent that the NIR methods are able to detect the differences of the maximum and minimum yield settings within one fraction and differences arising from the sampling times by the some variety of fractions. In our study, the flour samples were being monitored based on the sampling times by NIR equipment. Hereby we were able to get information about the stability of the same flour samples as the time goes by. It is a novel step to begin realisation of the on-line technique during the milling process.

In the future, a potential development could be checking and monitoring the ARF fractions on-line, using real-time NIR methods attaching to the quality system.

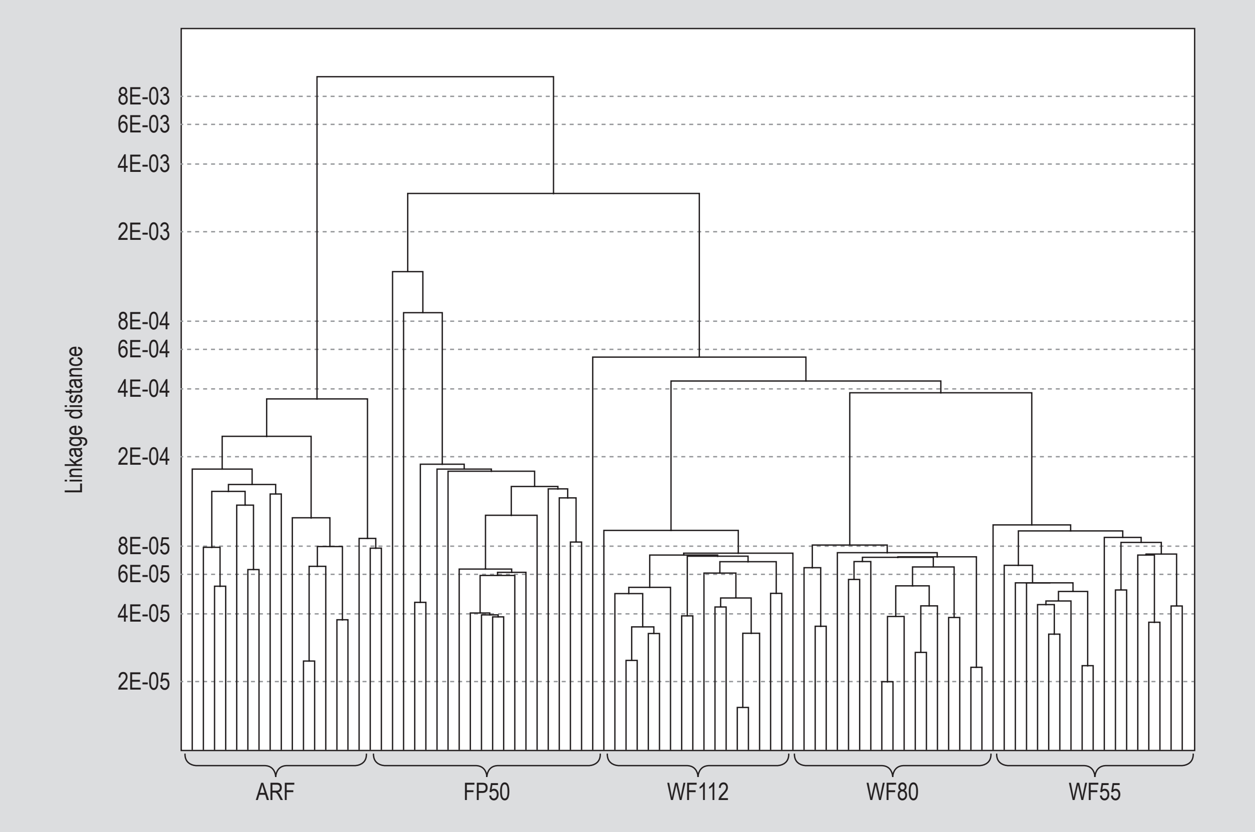

Figure 5. Dendrogram of the fractions (WF55, WF80, WF112, FP50, ARF) based on the second order derivatives (D2OD) 8/0 nm spectra during the second trial (WF = wheat flour; FP = flour for pasta; numbers refer to % ash content; ARF = aleurone-rich flour).

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