

Off-Line Detection of “Pannon Wheat” Milling Fractions by Near-Infrared Spectroscopic Methods

E. Izsó, M. Bartalné-Berceli, Sz. Gergely, A. Salgó

Abstract—The aim of this investigation is to elaborate near-infrared methods for testing and recognition of chemical components and quality in “Pannon wheat” allied (i.e. true to variety or variety identified) milling fractions as well as to develop spectroscopic methods following the milling processes and evaluate the stability of the milling technology by different types of milling products and according to sampling times, respectively. These wheat categories produced under industrial conditions where samples were collected versus sampling time and maximum or minimum yields. The changes of the main chemical components (such as starch, protein, lipid) and physical properties of fractions (particle size) were analysed by dispersive spectrophotometers using visible (VIS) and near-infrared (NIR) regions of the electromagnetic radiation. Close correlation were obtained between the data of spectroscopic measurement techniques processed by various chemometric methods (e.g. principal component analysis [PCA], cluster analysis [CA]) and operation condition of milling technology. It is obvious that NIR methods are able to detect the deviation of the yield parameters and differences of the sampling times by a wide variety of fractions, respectively. NIR technology can be used in the sensitive monitoring of milling technology.

Keywords—Allied wheat fractions, CA, milling process, near-infrared spectroscopy, PCA.

I. INTRODUCTION

WHEAT is one of the most important cereal food stuff from the aspect of nutrition, because grain crops are containing 60-70% carbohydrate, they are easy to store and process and they have wide range of use [1],[2]. The average composition of a wheat grain is 71.9%, 12.2%, 1.9%, 1.7% of starch, protein, non-starchy carbohydrate and ash, respectively [2]. Common wheat (*Triticum aestivum*) is generally classified as winter and spring wheat besides these more categories are existed according to the geographical effects in America but in Europe and also in Hungary diverse specification systems exist, that are based primarily on wheat quality parameters.

The main parameters of the wheat measurable by infrared spectrophotometers are moisture, protein, starch, wet gluten, ash content and rheological parameters [3]. The grain quality parameters varied significantly, even when they were harvested in the same field and at the same time [4]. On-line NIR devices allow the detection and improvement of grain and

cereal product quality indifferent processed products (i.e. grain, flour, bread, extrudates etc.) [5]-[7]. There are several reports which is examining flour mixtures, but these prefer to observe one kind of bakery products or raw materials. In contrast the main aim in our study is to monitor different fractions of flour, which were carried out simultaneously to highlight the variability of the different kinds of products according to the sampling times and different technology settings, respectively.

So NIR spectroscopy as Process Analytical Technology (PAT) tool [8] could be integrated into monitoring the milling process, which is an important system of controlling factory in terms of quality, stability and yields of the final product.

II. MATERIALS AND METHODS

A. Samples

The “Pannon wheat” [9] samples origin milling fractions were produced by Gyermelyi Corp. flour-mill (Gyermely, Hungary). The same silo was used during all feeding trials using so-called closed system milling process, and 300 tons of allied wheat (i.e. true to variety, variety identify) sharing genetic and environmental background were separated allowing the use of wheat flour of identical quality during all experiments. Two experiments were carried out. During the measurements the samples were examined according to two kinds of aspects. One aspect was to follow the time and hereby monitoring the stabilities of the fractions as the time goes by during the first trial. Another aspect was to evaluate the effects of the yields, how influence the changes of the fractions during the second trial. In both trials examined standard wheat flour fractions in compliance with Codex Alimentarius Hungaricus (BL55, BL80, BL112, TL50; where “BL” and “TL” are Hungarian abbreviation of wheat flour and flour for pasta, respectively and the number after abbreviation refer to the ash content in hundredth of %) and newly-developed experimental wheat flour, aleurone-rich flour (ARF) [10], [11]. The specifications of these fractions are contained in Table I. In the first trial, 42 samples were taken and by the second trial there were 30 samples with 3 parallel independent scanning by each samples and trials. The samples were collected according to the sampling time (i.e. 8AM, 12AM, 4PM, 8PM, Midnight and 4AM on the following day) in the first trial. During the second trial the first half of the day was dedicated to getting the maximum yield of the TL fraction, so sampling times were at 7AM, 10AM and 1PM. The second half of the day was aimed at getting the minimum yield of the TL fraction, so sampling times were at 3PM, 6PM and 9PM. The 5 fractions along with the TL were also examined during

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each approach.

TABLE I
COMPOSITION OF THE ALEURONE-RICH AND ENDOSPERM-RICH MILLING PRODUCTS [2], [11]

Ingredients	Aleurone-rich flour (ARF)	Endosperm-rich products (standard fractions)
	[% dry weight basis]	[% dry weight basis]
Moisture	-	-
Ash	3.83	1.7
Protein	26.67	12.2
Starch	47.65	71.9
Total Dietary Fibre	17.59	1.9
Crude Fat	4.26	1.9

B. Reference Materials

The reference materials for spectroscopic measurements were gluten from wheat, unmodified wheat starch and wheat germ oil originated from Sigma Chemical Co. (St Louis, MO, USA).

C. Spectroscopic Measurements

Samples and reference materials were scanned using dispersive NIR instrument (NIRSystems 6500 monochromator system; Foss NIRSystems, Inc., Silver Spring, MD, USA) fitted with a Rapid Content Analyser (RCA) and micro-sample cup equipped with threaded back to collecting the raw spectra. Samples were scanned from 400 nm to 2498 nm in reflectance mode (R mode: Si detector [400-1098 nm] and PbS detector [1100-2498 nm]). Spectral and reference data were processed using Vision 3.20 (Foss NIRSystems, Inc., Silver Spring, MD, USA), Microsoft Excel 2007 (Microsoft Corporation, Redmond, WA, USA), Statistica 11 (StatSoft, Inc., Tulsa, OK, USA) software packages. The first (D1OD) and second (D2OD) order derivatives were calculated from the raw spectra by gap-segment method. Raw VIS-NIR spectra were transformed into D2OD using 2/0 nm, 4/0 nm, 8/0 nm, 12/0

nm, 16/0 nm and 20/0 nm segment and gap size, respectively by Vision 3.20 software. The D2OD 8/0 nm gap-segment setting was applied in the case of each spectra and used multivariate data analysis such as principal component analysis (PCA) and cluster analysis (CA).

The PCA is a projection method that provides an interpretable overview of the main information contained in a multidimensional table. It takes the information carried by the original variables and projects them onto a smaller number of latent variables called principal components (PC) [12], [13]. By plotting PCs important sample and variable interrelationships can be revealed, leading to the interpretation of certain sample groupings, similarities or differences. The CA is an exploratory data analysis tool, the main aim of which is to sort the different objects into groups. CA observes the degree of association between objects and it is maximum if they belong to the same group and minimum the other way round [14].

III. RESULT

By both trials the deviations of the three standard fractions (BL55, BL80, BL112), TL50 fraction and the ARF fraction have already been appeared in the case of the raw spectra (data not shown). The huge baseline shift between the TL50, ARF and the other fractions are caused by two factors. Firstly, the ARF fraction has a higher aleurone content, than the BLs. In the 1100-2498 nm region the variance is derive from the disparate chemical properties, but in 400-1098 nm range the main variability in the visible range. Secondly, the TL50 fraction has bigger particle size than the other fractions (Table II). In this case the physical properties cause the deviations between the fractions, mainly in the NIR (1100-2500 nm) range.

TABLE II
DETAILS AND PARAMETERS OF THE MILLED PRODUCTS [10]

Quality characteristic	Milling products of <i>Codex Alimentarius hungaricus</i> (standard fractions)			
	BL55	BL80	BL112	TL50
Ash [% of dry matter]	at most 0.60	0.61-0.88	0.89-1.12	at most 0.50
Acidity at most	2.5	3.0	3.5	2.5
Moisture [%] at most	15.0	15.0	15.0	15.2
Wet gluten [%] at least	27	28	28	26
Particle size [µm]	100% undergoing at 315 µm and at least 95% undergoing at 250 µm		100% undergoing at 400 µm and at most 15% undergoing at 200 µm	

The D2OD 8/0 nm gap-segment setting was used to retain the sensitivity and get more informative peaks about the milling fractions. The range of 1700-1800 nm is highlighted in the case of the fractions [Fig. 1] and the reference materials [Fig. 2] too to compare the main components of the wheat flour (i.e. starch, protein and lipid). In Fig. 2 is shown the spectra of the reference materials. In this range the D2OD 8/0 nm spectra of the reference materials and the D2OD 8/0 nm spectra of the samples have high variability of main components, which are detectable. The D2OD 8/0 nm spectra of BL55, BL80, BL112 and TL50 fractions peak at 1748 and

1780 nm [Fig. 1] which represents starch [Fig. 2]. The ARF has absorption bands around 1725 and 1760 nm, which is appearing on the Fig. 1, owing to protein and lipid, and lipid respectively [Fig. 2]. Hereby the deviations of the BLs and TL50 and ARF fraction become obvious such as the assignation is reinforced. During the first trial the samples were constituted different groups according to the sampling times (i.e. 8AM, 12AM, 4PM, 8PM, Midnight and 4AM on the following day) in the priority range 1730-1765 nm (data not shown).

There are mainly shifts accordingly the sampling time in the

case of the D2OD 8/0 nm spectra of the BL112 (high bran amount) and the ARF fraction too (data not shown). Two kinds of fractions the BL112 and the ARF have only visible deviation based on the changes of sampling times, of this two flour samples have more sensitivity peaks of the main components in the 1700-1800 nm range, than the other three fractions (BL55, BL80 and TL50).

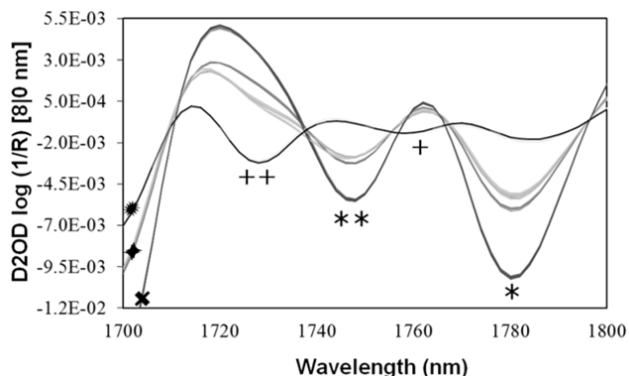


Fig. 1 D2OD 8/0 nm spectra of wheat flour fractions in the 1700-1800 nm wavelength range: x=TL50 fraction, ◆=BL55, BL80, BL112 fractions, *=ARF fraction and peaks of the main components: +/+ +=lipid, */**=starch

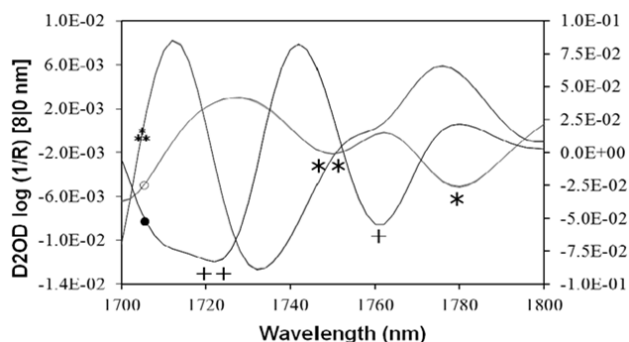


Fig. 2 D2OD 8/0 nm spectra of the reference materials in the 1700-1800 nm wavelength range: * =gluten from wheat, ○=unmodified wheat starch, ◆=wheat germ oil [lipid] and peaks of the main components: +/+ +=lipid, */**=starch

The applied PCA method in the range of 1100-2498 nm highlighted the differences according to the sampling times in the case of BL112 and the AFR fraction as shown in Figs. 3 and 4. The Pearson correlation values (r) were calculated between the first two loadings of PCA and the D2OD 8/0 nm spectra of the reference materials, in BL112 and ARF fraction. The starch correlate with the loadings of PC1 of BL112 ($r=0.9779$) and the loadings of PC2 of BL112 with protein ($r=0.4722$). In the ARF fraction the loadings of PC1 correlate with starch ($r=0.9449$) and the loadings of PC2 with protein ($r=0.3557$) and lipid ($r=0.3292$) content, respectively. The values of the correlations in the case of the ARF fraction are increased and due to the bigger lipid amount.

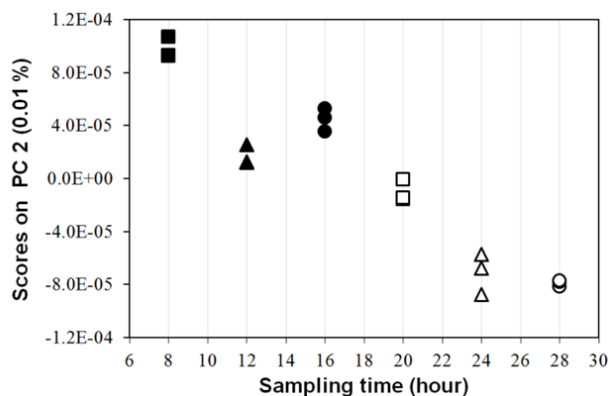


Fig. 3 The PC2 and sampling times score plot in the case of D2OD 8/0 nm spectra of the BL112 fraction during the first trial (sampling times: ■:8=8AM, ▲:12=12AM, ●:16=4PM, □:20=8PM, △:24=Midnight, ○:28=4AM on the following day)

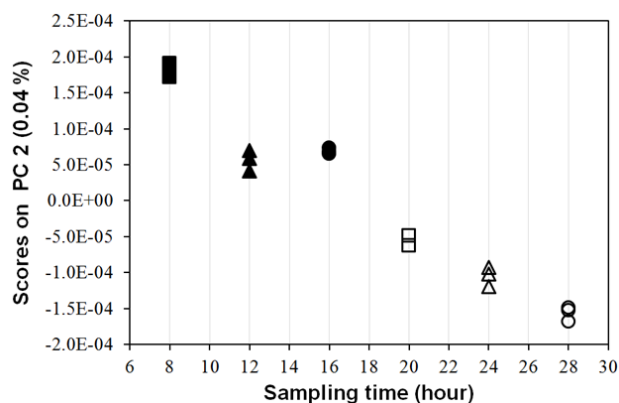


Fig. 4 The PC2 and sampling times score plot in the case of D2OD 8/0 nm spectra of the ARF fraction during the first trial (sampling times: ■:8=8AM, ▲:12=12AM, ●:16=4PM, □:20=8PM, △:24=Midnight, ○:28=4AM on the following day)

In the second trial the changes of the yields of TL were evaluated how influence the quality of other wheat flour fractions. The maximum and minimum yields of TL were compared with PCA methods in the case of BL55, BL80, BL112 and ARF fraction. The significant deviations are shown in Fig. 5. In the case of the BL112 fraction. The loading values of PC1 and PC2 in the case of the BL112 fraction showed systematic separation according to the first half of the day (i.e. the maximum yield of TL at 7AM, 10AM and 1PM) and second half of the day (i.e. the minimum yield of TL at 3PM, 6PM and 9PM), respectively [Fig. 5]. In the case of the ARF fraction the loading of PC1, there was no so sharp separation according to the sampling times, compared to the BL112 fraction (data not shown). The changes of the settings were clearly reflected in the case of the loading of PC2 of the ARF fraction. This two fractions such as during the first trial are very sensitive for the chemical components changes and the yields settings too. The minimum yield of TL causes reduced starch content and the maximum yield of TL results increased trend. On the CA dendrogram all fractions

were separated, first of all the ARF fraction with different chemical content and after that the TL50 with bigger particle size and finally the rest of the BL fractions, which were very similar (data not shown).

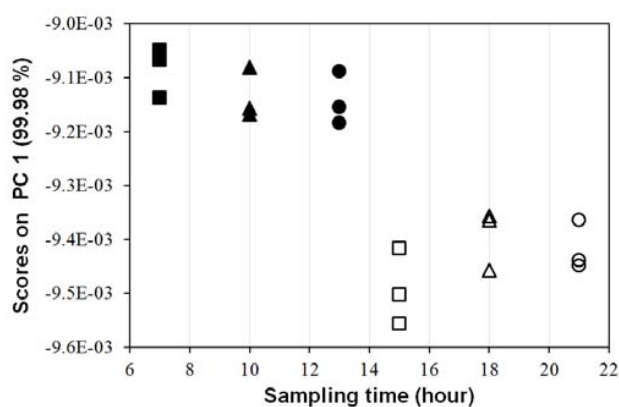


Fig. 5 The PC1 and sampling times score plot in the case of D2OD 8/0 nm spectra of the BL112 fraction during the second trial (sampling times: ■:7=7AM, ▲:10=10AM, ●:13=1PM maximum yield of the TL and □:15=3PM, △:18=6PM, ○:21=9PM minimum yield of TL)

IV. CONCLUSION

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 TL50 fraction in the case of all trials separated well from the rest of the BL fractions. In the case of the ARF fraction colour caused major variability (besides the obvious difference in composition), because it has higher aleurone amount than the BL fractions, while the TL50 fraction distinct due to the particle size. The flour samples were monitoring according to the sampling times by NIR equipment, hereby were getting information about the stability of the same flour samples versus the milling times.

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