Food Chemistry 195 (2016) 49–55

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Differentiation of rye and wheat flour as well as mixtures by using the kinetics of Karl Fischer water titration

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ARTICLE INFO

Article history:
Received 30 November 2014
Received in revised form 15 June 2015
Accepted 24 August 2015
Available online 2 September 2015

Keywords:
Karl Fischer water titration
Rye
Wheat
Flour
KFT kinetics

ABSTRACT

The aim of this study was to find a simple way to differentiate between rye and wheat flour and their mixtures by using the kinetic parameters of Karl Fischer water titration (KFT). Consequently, the water content and type of molecules in rye and wheat mixtures used in Romanian bread making have been investigated by means of volumetric KFT. Further, the kinetics of KFT have been determined and novel kinetic parameters corresponding to "surface" and "strongly-retained" water molecules have been identified to discriminate between rye and wheat flour and their mixtures. The "surface" and "strongly-retained" water reaction rates well correlate with the rye content in the flour mixtures, especially at higher temperature analysis ($r > 0.95$). These parameters can be used as indicators for quality evaluation of such type of mixtures, as well as to identify adulteration by improper use of the rye–wheat flour ratios in bread making.

1. Introduction

Wheat is one of the most cultivated cereal, the crops covering approximately one third of the world's total cereal cultivation (Belitz, Grosch, & Schieberle, 2009). On the other hand, rye is cultivated at 2% all over the world, especially in Europe. Both are the two cereals mostly used for bread making (Andersson, Dimberg, Åman, & Landberg, 2014). Due to the higher content of fibre, lower level of fat and storage proteins, rye is a more valuable raw material (Buksa, Nowotna, Ziobro, Gambu, & Kowalski, 2012; Goesaert et al., 2005; Pareyt, Finnie, Putseys, & Delcour, 2011). Wheat and rye flour are two of the most used ingredients for bread making. The first is the most disposable while the second has other advantages, which are principally due to the differences in composition (Belitz et al., 2009). The most important difference appears in the protein composition. The prolamine and glutenin (as well as gluten) content is higher in wheat flour, while the albumins content is higher in rye flour (Buksa et al., 2012; Doblado Maldonado, Pike, Sweley, & Rose, 2012; Goesaert et al., 2005). Furthermore, the content of pentosans is four times higher in rye flour (6–8%) than in wheat flour (Buksa et al., 2012). Among other bioactive compounds, alkylresorcinols that have important health benefits, are found in more than double content in rye flour in comparison with wheat flour (Andersson, Amana, Wandel, & Frølich, 2010; Andersson et al., 2014). An important difference between wheat and rye is the gluten content, which is higher in wheat flour (Goesaert et al., 2005; Li Vigni, Baschieri, Marchetti, & Cocchi, 2013). Despite its insolubility and hydrophobic nature, gluten absorbs approximately twice its dry weight of water (Wieser, Koehler, & Konitzer, 2014). Thus, gluten is mainly responsible for the holding of a significant amount of water, as well as for the specific rheological properties of dough (Belitz et al., 2009; Goesaert et al., 2005). The hygroscopicity of wheat flour and bran is mainly due to the presence of starch and gluten that allow releasing the "compartmentalised water". It was demonstrated by DTA analysis that the distribution of free and bound water was altered and the water release prolonged in bran-enriched wheat flour (Roozendaal, Abu-hardan, & Frazier, 2012). Furthermore, water unextractable arabinoxylans have a strong tendency to bind water, but endogenous arabinoxylans immobilising some of the water necessary for hydration of gluten proteins and could have interferences in interactions between the gluten proteins (Duyvejonck, Lagrain, Pareyt, Courtin, & Delcour, 2011; Van Der Borght, Goesaert, Veraverbeke, & Delcour, 2005). The protein content, the ratio of damaged starch during milling as well as the

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http://dx.doi.org/10.1016/j.foodchem.2015.08.124
0308-8146/

proportion of non-starch carbohydrates determines the water absorption by flour (Ma et al., 2007; Roozendaal et al., 2012; Saad et al., 2009). Starch granules can absorb up to 50% of their dry weight of water and an important part is damaged during milling (Goesaert et al., 2005). The flour composition is strongly related to its water content, force of water binding, water absorption and water holding capacity. Consequently, water content is one of the most important parameters for flour stability, processability and dough/bread properties (Aponte et al., 2014; de la Hera, Rosell, & Gomez, 2014; Fessas & Schiraldi, 2005; Garcia Alvarez et al., 2006; Joye, Lagrain, & Delcour, 2009; Pareyt & Delcour, 2008; Roozendaal et al., 2012). The water content in flour up to 14% prevents the microbial spoilage and reduces the kernel metabolism (Corpaş et al., 2014; Pareyt & Delcour, 2008). On the other hand, water is important in the milling process of cereals (separation of starch) where the water content must be a little higher for a better separation of the starchy endosperm cells (Doblado Maldonado et al., 2012; Hsu, Lu, Chang, & Chiang, 2015; Ma et al., 2007). As a result, the flour quality strongly depends (indirectly or directly) on the water content and on how strongly water is bound to components in the flour.

The correct determination of water content and types of water molecules in rye and wheat flour mixtures (principally used for bread making) is very important from the quality and human health point of view. There are two method groups used for determination of water content and/or moisture content in food products. Primary methods directly measure the true water content. They are based on the physical separation of water by distillation or drying techniques (oven, infrared or microwave drying) as well as on quantitative and selective chemical reactions with water (Karl Fischer titration, production of acetylene or hydrogen). Secondary methods (nuclear magnetic resonance spectroscopy, NMR, near-infrared spectroscopy, NIR, microwave techniques, densitometry, polarimetry, refractometry, etc.) furnish more or less accurate values for water content, being based on various properties that depend on water content (Isengard, 1995, 2001; Isengard & Färber, 1999; Isengard, Kling, & Reh, 2006; Yazgan, Bernreuther, Ulberth, & Isengard, 2006). There are many disadvantages of some techniques related to selectivity to water, accuracy and precision, time required or the equipment, energy and consumables involved in the analysis (e.g. oven drying methods, the oldest methods, are not selective to water, are time-consuming and energy-intensive, and decomposition can occur; secondary methods need very specific calibrations for various food products (Isengard, Merkh, Schreib, Labitzke, & Dubois, 2010) and most of them need expensive equipment). Chemical methods such as Karl Fischer titration allow determining the true and total water content. They are selective to water, the analysis conditions can be chosen according to food product characteristics and stability (especially the temperature, which can be lowered for very sensitive food samples), the measurement time is only few seconds to minutes and the equipment and consumables are cheap. Another difficulty for a correct water determination by classical and standardised methods (especially drying methods) is related to the term used ("water content" or "moisture content"). From the scientifically point of view, it is very clear that chemical methods are more simple, accurate, and cheaper (Isengard, 2008; Merkh, Pfaff, & Isengard, 2012; Schmitt & Isengard, 1998). Furthermore, only few methods allow discriminating between "surface" and "strongly-retained" water molecules (Hădărugă, Hădărugă, & Isengard, 2013; Isengard & Heinze, 2003). One of these methods is Karl Fischer water titration (KFT). It is based on a redox reaction of water, iodine and methyl sulphite in presence of an organic base. Depending on the sample types, specific modifications of the KFT method have been developed (e.g. mono- and bi-component volumetric KFT, coulometric KFT as well as various mechanical and electrical parameters) (Hădărugă, Hădărugă, Bandur, & Isengard, 2012; Kestens, Conneely, & Bernreuther, 2008; Merkh et al., 2012; Schmitt & Isengard, 1998; Wang et al., 2012). Such KFT techniques, even volumetric or coulometric, have been recently evaluated for their capability to determine the true water content of rye and wheat flour samples (as reference materials) (Kestens et al., 2008; Schmitt & Isengard, 1998) or other reference material samples (Ducat, Felsner, da Costa Neto, & Quináia, 2015; Merkh et al., 2012; Ronkart et al., 2006; Wang et al., 2012).

Our studies were focused on the differentiation of rye–wheat flour mixtures that are mainly used for bread making of fibre-enhanced food products in Romania. In this context, the highly selective to water method namely Karl Fischer water titration, KFT, have been used. A novel approach on the discrimination between "surface" and "strongly-retained" water based on KFT kinetics have been proposed. Furthermore, the accuracy of this approach was evaluated by means of correlations of these parameters with the flour composition at various temperatures.

2. Materials and methods

2.1. Materials

Rye flour was obtained from the Romanian market. According to the producer, it had the following characteristics: whole grain rye (*Secale cereale* L.) flour, protein content 9.0 g/100 g, carbohydrates 67.8 g/100 g, lipids 1.3 g/100 g, fibres 7.7 g/100 g, ash content max. 1.20% and moisture max. 14% (by oven drying method). The wheat (*Triticum aestivum* L.) flour had the same provenience and the main characteristics (according to manufacturer) were protein content 10.7 g/100 g, carbohydrates 73.1 g/100 g, lipids 0.9 g/100 g, fibres 1.3 g/100 g, and ash content of max. 0.48%. Eleven rye–wheat flour mixtures containing 0–100% rye flour have been obtained by mechanical mixing (codes P1–P11, Table 1). The bi-component KFT technique works with a component 1 as titrating solution (Hydranal®-Titrant 5, Sigma–Aldrich, Buchs, Switzerland) and a component 2 as working medium (Hydranal®-Solvent that contains a solution of sulphur dioxide and imidazole in methanol, Sigma–Aldrich, Buchs, Switzerland). The titre of the component 1 was determined by using the Hydranal®-Water standard 1.0 (solution of water in methanol, 10.00 mg H_2O/g) from Sigma–Aldrich (Buchs, Switzerland).

2.2. Karl Fischer water titration (KFT)

The bi-component volumetric KFT technique has been used for determining of water content as well as for evaluating the "surface" and "strongly-retained" water in the rye–wheat flour mixtures by using KFT kinetics. KFT was carried out by using a KF 701 Titrino apparatus (Metrohm, Herisau, Switzerland) equipped with a 10-mL dosing system and a 703 Ti Stand stirring system

Table 1
Rye–wheat flour samples and water concentration determined by KFT (the number of replicates is presented in parenthesis).

No.	Code	Rye flour (%)	Water (%) (at 25 °C)	Water (%) (at 40 °C)
1	P1	0	13.97 ± 0.39 (8)	14.21 ± 0.35 (7)
2	P2	10	13.87 ± 0.36 (8)	13.94 ± 0.18 (6)
3	P3	20	14.14 ± 0.31 (8)	13.97 ± 0.42 (6)
4	P4	30	13.76 ± 0.41 (6)	13.70 ± 0.33 (7)
5	P5	40	13.91 ± 0.60 (7)	12.97 ± 0.20 (7)
6	P6	50	12.98 ± 0.61 (6)	13.29 ± 0.20 (7)
7	P7	60	12.89 ± 0.46 (6)	13.10 ± 0.37 (8)
8	P8	70	12.89 ± 0.62 (7)	12.68 ± 0.41 (7)
9	P9	80	12.71 ± 0.86 (6)	12.45 ± 0.27 (7)
10	P10	90	12.12 ± 0.42 (8)	12.58 ± 0.45 (8)
11	P11	100	11.52 ± 0.46 (8)	11.99 ± 0.39 (7)