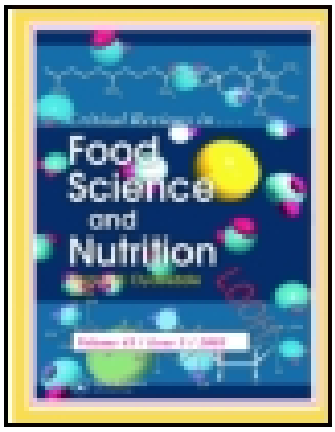

Critical Reviews in Food Science and Nutrition
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/bfsn20

Quality and Safety Aspects of Cereals (Wheat) and Their Products

Theo Varzakas[a]
[a] Technological Educational Institute of Peloponnese, Kalamata, Greece
Accepted author version posted online: 01 Apr 2015.

To cite this article: Theo Varzakas (2015): Quality and Safety Aspects of Cereals (Wheat) and Their Products, Critical Reviews in Food Science and Nutrition, DOI: 10.1080/10408398.2013.866070

To link to this article: http://dx.doi.org/10.1080/10408398.2013.866070

Quality and Safety Aspects of Cereals (Wheat) and Their Products

THEO VARZAKAS

Technological Educational Institute of Peloponnese, Kalamata, Greece

Address correspondence to Theo Varakas, Technological Educational Institute of Peloponnese, Kalamata 24100, Greece. Email: tvarzakas@teikal.gr

Abstract

Cereals and most specifically wheat are described in this chapter highlighting on their safety and quality aspects. Moreover, wheat quality aspects are adequately addressed since they are used to characterize dough properties and baking quality. Determination of dough properties is also mentioned and pasta quality is also described in this chapter. Chemometrics-multivariate analysis is one of the analysis carried out. Regarding production weighing/ mixing of flours, kneading, extruded wheat flours, and sodium chloride are important processing steps/raw materials used in the manufacturing of pastry products. Staling of Cereal-Based Products is also taken into account. Finally, safety aspects of cereal-based products are well documented with special emphasis on mycotoxins, acrylamide, and near infra red (NIR) methodology.

Keywords: Cereals, Safety, Quality, Pastry Products, Wheat Flour

INTRODUCTION

Pastry products comprise a big category of food products in Greece. They are produced as frozen and their main raw material is wheat flour. The main items consist of bakery, biscuit and confectionery products..

Wheat flour can form the dough, which is elastic, under appropriate conditions. Soft wheat (*Triticum vulgare*) is used in the production of bakery flour and covers more than 90% of world production. Flour must be purchased from approved suppliers. Cereals are constituted mainly of starch (75%) protein (15%) and fat (3%). However, they also contain minerals, bioactive phytochemicals (lignans, sterols, alkylresorcinols, phenolic acids) antioxidants and vitamins (folate, tocotrienols) in various concentrations, which are the primary reasons of cereal quality (Papageorgiou and Irakli, 2003; Juntunen et al., 2000; Ragaee et al., 2005).

Cereals are also rich in dietary fibers, trace elements, and micro-nutritional constituents like phytoestrogens and antioxidants which are very important in disease prevention. The major part of these ingredients, approximately 65-85%, is found in the barn and in the sperm.

The polysaccharides of cereals have been shown to have beneficial effects on nutrition and health. The non-starch polysaccharides are the major components of dietary fibre in cereal grain.

Moreover, the species composition of a cereal-based food is a key factor in determining the quality and safety of the final product (Terzi, 2005).

Organoleptic quality is also very important in cereals representing the choice of consumers (appearance, texture, taste, freshness). This is strongly linked with food safety aspects and hence

in this chapter we will try to see the link between quality and safety of cereal products with strong emphasis on wheat flour.

Wheat quality

Wheat quality could be considered in terms of yield, resistance to stress conditions and selling price for the side of the farmer, whereas for the miller or the processor, quality is protein content, flour yield, baking performance or pasta quality and regarding the consumersô point of view wheat quality has to do with taste, nutrition and safety.

The most important quality property is the gluten strength. When flour is mixed with water a protein nexus is formed due to precipitation of two proteins glutenin and gliadin. The glutenin polymerizes forming an elastic nexus, while the gliadin is incorporated into a sticky extensible mass entering into the nexus of gluten, so that the dough becomes more extensible and flexible. The strong flours absorb the carbon dioxide, produced during the ripening of the dough thus resulting in even more inflated bread (Varzakas and Arvanitoyannis, 2007). The type and quantity of the gluten proteins are important in determining the bread making properties of the wheat flour (Dupont and Altenbach, 2003; Gomez *et al.* 2011). The gluten plays a vital role in determining the appearance and crumb structure of cereal-based products (Demirkesen *et al*. 2010). Flour quality depends on a specific balance between gliadin and glutenin and for bread making, an appropriate balance between dough viscosity and elasticity/strength is required (Khatkar *et al.* 1995). Insufficiently elastic gluten leads to low bread loaf volume. Increased elasticity leads to higher loaf volume. During mixing, glutenins tend to align and form cross-links between glutenin molecules leading to an increase in dough strength. The amount of

glutenin in flour has been found to be positively correlated with dough strength (MacRitchie, 1992) while gliadin promotes elongational resistance and dough extensibility (Song and Zheng, 2008). Barak *et al*. (2013) selected four wheat varieties to study the contribution of gliadins and glutenins to the dough rheological parameters, pasting profile and bread quality. The results showed that gliadins, glutenins and Gli/Glu ratio had appreciable effects on the dough stability, dough development time, peak viscosity, breakdown viscosity, bread specific volume and crumb firmness. Glutenins observed a strong negative relation with peak viscosity, breakdown viscosity and pasting temperature while gliadins showed positive association with breakdown viscosity, setback and final viscosity. Gli/Glu ratio was negatively correlated with dough development time (r=-0.988), dough stability (r =-0.940), gluten index (r=-0.975) and protein content (r=- 0.837). Protein (r = 0.826), gluten index (r = 0.557), gliadins (r = 0.546) and glutenins (r = 0.939) exhibited positive correlations with bread specific volume. However, higher Gli/Glu ratio was found to be adversely affecting the bread volume and crumb firmness suggesting the importance of a balance of both the gluten subfractions for enhanced bread quality. The results suggested that gliadins are equally important as glutenins in asserting the bread making performance of wheat varieties.

Dough properties are largely dependent on hydrated gluten protein, as it becomes, when dough is formed, a phase giving rise to a viscoelastic behaviour (Anjum *et al.* 2007). Moreover, strength and elastic properties are mainly imparted by the glutenin fraction, whilst gliadin fractions can play a role in determining dough extensibility (Anjum *et al.* 2007). Gupta *et al.* (1993), Singh and MacRitchie, (2001) have focused on the application of theories from polymer science to the gluten/dough system. They have seen it as a polymeric system, where visco-

elasticity arises from the extension of polymer chains between entanglement points and the resistance to extension depends on the entanglement network density. Other Author (Belton, 2005) postulate a óloop and trainô mechanism, where the high molecular weight (HMW) glutenin subunits form high molecular mass polymers stabilised by disulphide bonds which represent the óbackboneô of gluten, and a significant contribution to the elastic properties is given by extensive arrays of interchain hydrogen bonds formed by other sub-units.

There are many parameters used to characterize dough properties and baking quality of wheat: Zeleny sedimentation test, falling number, hardness binding capacity, alveograph, farinograph, extensograph and mixograph parameters (Belderok *et al.* 2000).

Bread wheats are classified as hard or soft, according to their hardiness. Bread wheats are further divided according to their appearance, cultivar, protein content and falling number. Hard wheats are used for bread production. They contain low yellow pigment content and for bread making they should have seed protein levels higher than 11.5%. Cultivars exhibiting specific dough strength and mixing time combinations are favored by bakers. Hard wheats are also used for the production of Asian noodles, flat bread, manufactured starch and gluten. Soft wheats are characterized by low protein content and are used for cakes, sweet biscuits and pastries. For cracker biscuits, hard wheat flour with higher protein content is used. The soft wheat market is smaller than the corresponding hard wheat market (Varzakas and Xynias, 2013). A hard wheat grain always requires greater pressure for disintegration compared to a soft wheat grain.

Durum wheats are mainly used for producing Italian style pasta products, i.e. spaghetti, macaroni, etc. For pasta production, durum wheat cultivars with high protein content and yellow pigment are preferred. The durum grains are milled to result to a coarser texture compared to the

respective for bread and cake production, producing semolina. The semolina value of durum wheat is determined by: (a) net semolina production, (b) total product of semolina processing, (c) semolina granulation, (d) pureness, (e) colour, and (f) ability in resulting end product with appropriate quality (Liakopoulou-Grivakou, 2004). Pasta color is controlled by certain individual traits of durum wheat. Net semolina production, flour and flour as a percentage of the total semolina production depend on the genotype and are influenced by the environment (Liakopoulou-Grivakou, 2004).

Durum wheat (*Triticum turgidum* L. ssp. durum) is cultivated mainly in the Mediterranean Basin and North America, in irrigated and rainfed environments. It possesses harder kernel, considerably higher yellow pigment content, and relatively higher grain protein content than common wheat (*Triticum aestivum* L.). Durum wheat generally has inextensible gluten (Ammar *et al.* 2000). Yellow pigment content, protein content, and gluten strength play a critical role in determining the pasta-making quality of durum wheat (Edwards et al. 2003). Durum wheats frequently experience drought and/or heat stress in the SEWANA region (South Europe, West Asia, and North Africa), where they are mainly grown under rainfed conditions. Heat and drought stress, particularly during the grain filling period, often limit the expression of yield potential, may enhance grain protein content, and may improve or deteriorate processing quality.

When breeding for durum wheat quality, the sodium dodecyl sulphate sedimentation (SDSS) test is commonly used to predict gluten strength (Brites and Carrillo, 2001; Peña *et al.* 1994). Other rapid gluten strength-related screening tests exist but these are applied mainly to common wheat. The lactic acid retention capacity (LARC) test was designed to estimate gluten

strength of soft wheat (Gaines, 2000), and it was highly positively associated with gluten strength parameters of Farinograph and Mixograph (Ram *et al.* 2005). The swelling index of glutenin (SIG) was recently developed for estimating insoluble glutenin content, and can be used for predicting gluten strength (Wang and Kovacs, 2002 a,b). Li *et al*. (2013) examined the effects of drought and heat stress conditions on grain yield and quality parameters of nine durum wheat varieties, grown during two years (2008-09 and 2009-10). Generally, G and E showed main effects on all the parameters whereas the effects of G x E were relatively small. More precipitation in Y09-10 may account for the large differences in parameters observed between crop cycles (Y08-09 and Y09-10). Combined results of the two crop cycles showed that flour protein content (FP) and SDS sedimentation volume (SDSS) increased under both stress conditions, but not significantly. In contrast the gluten strength-related parameters lactic acid retention capacity (LARC) and mixograph peak time (MPT) increased and decreased significantly under drought and heat stress, respectively. Drought and heat stress drastically reduced grain yield (Y) but significantly enhanced flour yellowness (FY). LARC and the swelling index of glutenin (SIG) could be alternative tests to screen for gluten strength. Genotypes and qualtiy parameters performed differently to drought and heat stress, which justifies screening durum wheat for both yield and quality traits under these two abiotic stress conditions.

Drought and high temperature are especially considered as key stress factors with high potential impact on crop yield. Yield safety can only be improved if future breeding attempts will be based on the valuable new knowledge acquired on the processes determining plant development and its responses to stress. Plant stress responses are very complex. Interactions

between plant structure, function and the environment need to be investigated at various phases of plant development at the organismal, cellular as well as molecular levels in order to obtain a full picture. The results achieved so far in this field indicate that various plant organs, in a definite hierarchy and in interaction with each other, are involved in determining crop yield under stress (Barnabas *et al.* 2008).

Spring wheat (*Triticum aestivum* L. cv. Triso) was grown by Brunnbauer et al. (2013) in a free-air carbon dioxide (CO_2) enrichment (FACE) system at Stuttgartï Hohenheim (Germany) in 2008 to examine effects on crop yield and grain quality. Elevated CO_2 had no significant impacts on aboveground biomass and grain yield components except for an increase in thousand grain weight by 5.4% with size distribution shifted towards larger grains. Total grain protein concentration decreased by 7.9% under CO_2 enrichment, and protein composition was altered. Total gliadins and their single types (ɤ 5-gliadins, ɤ 1,2-gliadins, Ŭ-gliadins, and ɔ-gliadins) were reduced, while albumins/globulins, total glutenins and their subunits were not influenced.

The gluten proteins (gliadins plus glutenins) were lowered by 11.3% in the high-CO_2 treatment, whereas proportions of gluten protein types were slightly affected as only ɤ 1,2-gliadins decreased. Accordingly, all proteinogenic amino acids were decreased by 4.2 to 7.9% in concentrations per unit flour mass, although partly below the level of statistical significance. In contrast, the composition of amino acids on a per protein basis remained unaffected except for a decline in serine. Among the minerals, the concentrations of calcium, magnesium, iron and cobalt decreased, while an increase was observed for boron. The concentrations of total non-structural carbohydrates and starch decreased, whereas fructose, raffinose and fructan increased. Total lipid concentration remained unaffected by the CO_2 enrichment, whereas the grain

carbon/nitrogen relation was increased by 8.5%. Implications may occur for consumer nutrition and health, and for industrial processing, thus breeding of new wheat cultivars that exploit CO_2 fertilisation and maintain grain quality properties is regarded as one potential option to assure the supply chain for the future.

Previous experiments under field conditions demonstrated that several grain quality traits are not affected by elevated CO_2 whereas other authors found evidence for serious impacts. The latter studies reported that especially compounds containing nitrogen (N) were decreased in grains under CO_2 enrichment (Wieser *et al.* 2008; Høgy *et al.* 2009, 2010), with both beneficial and adverse consequences for nutritional dietary value and processing quality.

Armanino et al. (2003) determined the percentages of methyl esters of the differently unsaturated fatty acids with 18-carbon atoms, of sterol fraction and of the other components i.e the lipid components of wheat in order to differentiate between *Triticum durum* and *Triticum aestivum*. They also applied chemometric methods in order to measure the classification and prediction abilities of the determined components of the lipid fraction of wheat in differentiating among species, origins, varieties and crops.

Demirozu and coworkers (2003) determined the levels of iron, copper, zinc, lead and cadmium, which are very important metals for human health and food quality, in bread samples obtained from 20 bakeries in Ankara and Samsun, Turkey. The atomic absorption spectrophotometry method was used to determine the concentration of these metals. No significant differences were found in copper and lead levels of samples obtained from bakeries in general, and in copper and cadmium levels of the samples from different provinces, while they

were considered significant in iron, zinc, and cadmium levels of samples in general, and in iron, zinc and lead levels of samples from different provinces.

Barley (*Hordeum vulgare*) is an important crop in northern parts of the world due to its early maturing ability. On a worldwide basis, only about 5% of the barley production is used for food (FAO, 2001), while most is used in the feed industry. The dominating fibres components in barley are the b-glucans and the arabinoxylans. Barley has the same or even higher fibre content as other cereals, and is recognised for its nutritive and health potential.

Holtekjølen et al. (2006) analyzed 39 varieties of diverse genetic origin of barley varieties, in order to classify them into groups of different chemical grain quality. They determined various chemical parameters (starch, amylose, protein, non-starch polysaccharides, b-glucan, arabinoxylans, degree of branching in arabinoxylans, arabinogalactan, cellulose) with emphasis on polysaccharides. The results showed that barley varieties have a wide diversity in polysaccharide content and composition.

Ragaee et al. (2005) evaluated four cereals including barley, pearl millet, rye and sorghum, which are adapted to the growing conditions in the United Arab Emirates, in terms of their composition of dietary fiber, resistant starch, minerals and total phenols and antioxidant properties. The adapted grains exhibited better nutritional quality compared to commercial hard and soft wheat flours, the main ingredients in grain-based food products.

Wheat genotype and genetic locci

Whatever is the approach to define quality its constituents are traits that are genetically controlled which can be measured by various biochemical, molecular and chemical tests.

Although, the hardness of a certain wheat variety can be genetically controlled, is not directly linked to the protein content of the grain (Simmonds, 1974; Miller *et al*, 1984; Huifen and Hoseney, 1991; Weegels et al. 1996).

Ghirardo et al. (2005) used matrix-assisted laser desorption/ionisation time-of-flight mass spectrometry and multivariate data analysis for the determination of wheat quality at different stages of grain development. Wheat varieties with one of two different end-use qualities (i.e. suitable or not suitable for bread-making purposes) were investigated. The samples were collected from grains from 15 until 45 days post-anthesis (dpa). Gluten proteins from wheat grains were extracted and subsequently analysed by mass spectrometry. Discrimination partial least-squares regression and soft independent modelling of class analogy were used to determine the quality of new and unknown wheat samples. With these methods, they predicted correctly the end-use qualities at every stage investigated. This new fast technique, based on the rapidity of mass spectrometry combined with the objectivity of multivariate data analysis, offers a method that can replace the traditional rather time-consuming ones such as gel electrophoresis. This study focused on the determination of wheat quality at 15 dpa, when the grain is due for harvest 1 month later.

The influence of wheat genotype and protein content and size distribution (Faergestad *et al.* 2004; Uhlen *et al.* 2004) on dough rheology; the effect of protein quality and content in interaction with other baking factors on bread characteristics (Aamodt *et al.* 2005), or the relationship between gluten quality and dough properties and performance (Marchetti *et al.* 2012) are also important factors to be considered.

A number of genetic loci are known to affect quality traits in bread wheat. As detailed in a review by Gale (2005), these include the Glu-1 loci on the long arms of homeologous group 1 chromosomes (encoding high-molecular-weight glutenin subunits (HMW-GS)), the Glu-3 loci on the short arms of group 1 chromosomes (encoding lowmolecular-weight glutenin subunits (LMW-GS)), and gliadin loci on the short arms of group 1 (closely linked with the LMW-GS loci) and 6 chromosomes. Genotypes in these protein coding regions have been used as predictors of dough rheology (Payne *et al.* 1987). Puroindoline genes at the Ha locus on the short arm of chromosome 5D are the main determinants of grain texture (Morris, 2002). Serpin proteins encoded at a locus on the long armof chromosome 5B, have been shown to affect milling yield (Cane et al. 2008).

Quantitative trait loci (QTLs) for wheat quality traits have been mapped (e.g., Groos et al. 2007; Kuchel *et al.* 2006; Mann *et al.* 2009; Radovanovic *et al.* 2002; Raman *et al.* 2009), based on the analysis of grain harvested from trials that had been conducted under favourable conditions. Maphosa *et al*. (2013) used grain produced in water-limited environments. Grain samples harvested from a mapping population grown in field experiments at two locations in Australia were used to assess characteristics of the grain, flour, dough and bread. Quantitative trait loci (QTLs) were mapped. The parents of the population, RAC875 and Kukri, differ at several loci that are known to affect grain quality or plant phenology. Of these, a high-molecular-weight glutenin locus (Glu-B1) affected dough properties, the puroindoline-encoding Ha locus affected grain hardness, flour and loaf properties and a photoperiod response locus (Ppd-D1) affected flour extraction and protein content. Similarly, several previously reported quantitative trait loci (not associated with specific genes) also had effects in the stress environments used here. In

addition, novel loci were detected for bread wheat quality traits; their effects may be specific to materials grown in water-limited environments.

Variations in the accumulation and structure of amount and size distribution of polymeric proteins (ASPP) in the wheat grain during the grain maturation period (GMP) are influenced not only by individual genetic (G) and environmental (E) factors, but also by the interactive effects of these factors (Johansson *et al.* 2005; Wieser and Seilmeier, 1998). Wheat development time, nitrogen (N) availability and temperature are the most important factors determining protein composition in mature wheat (Johansson *et al.* 2008; Malik *et al.* 2011; Stone and Nicolas, 1996b). However, the relative importance of G and E and how they interact to determine the protein composition of the mature wheat is not still clear.

The cultivar determined development time (CDDT), together with the amount and timing of N application, played a significant role in determining the accumulation and final composition of the wheat grain proteins, explaining 21-59% of the variation according to Malik *et al.* (2013). At low temperature, N application both at spike formation and at anthesis explained the highest proportion of variation (36%) in the percentage of sodium dodecyl sulphate (SDS) unextractable polymers in the total amount of polymers (% UPP), while at high temperature CDDT contributed most to the variation in % UPP (20%). The largest contributor to variation in the amount of total SDS extractable proteins (TOTE) was N application at anthesis, both at low and high temperatures (12% and 36%, respectively). Thus, the climate should be considered in recommendations for improving the protein quality and thereby the bread-making quality of wheat.

Tsilo *et al*. (2013) identified quantitative trait loci (QTL) influencing water absorption and dough rheological properties of hard red spring wheat. QTL were mapped on a genetic linkage map that comprised 531 simple sequence repeats (SSRs) and diversity array technology (DArT) marker loci. Composite interval mapping with 139 recombinant inbred lines (RILs) was used to identify QTL within and across two field environments. Six QTL on chromosomes 1A, 1B, 4B, 4D, and 5A were detected for farinograph water absorption. These QTL also confirmed earlier studies that flour water absorption is a function of protein content, starch damage, and gluten strength. In this study, dough rheological properties such as dough development time, dough

stability, mixing tolerance index, and time to breakdown were influenced by the high-molecular weight glutenin genes Glu-B1 and Glu-D1.

Other quality parameters

Another equally important quality parameter is the average of damaged amylococci during grinding. The latter are hydrolyzed by amylolytic enzymes over the ripening of the dough, thus providing the yeast with fermented sugar until the last inflation. The receiving of flour is a critical step because presence of defective flour means that the final product will be probably unsafe for the consumer (Varzakas, 2011). Moreover, high temperatures and excessive moisture in stored grains or high humidity under ambient storage conditions permit the proliferation of insects and molds, which cause large losses of qualitative, nutritional and hygienic nature. Therefore, the main reasons that cause grain quality degradation in the world are the following: over drying (cracking of seed), grain respiration (weight loss ï quality degradation), damages

due to insects and rodents infection (weight loss), mold and other bacterial contamination (mycotoxin quality degradation) (Kazazis, 1980, Wilcke *et al.* 2000).

Iconomou *et al*. (2006) evaluated the quality of certain cereal grains under controlled and/or modified storage conditions. Cereal grains of corn and wheat were stored under controlled atmospheric conditions of 2% and 8% O_2 for 12 and 6 months time periods, respectively. They showed that storage under high nitrogen atmospheric conditions kept the flour acidity stable for all the storage period and enhanced the germination ability of grains. Finally inhibition of the existing entomological and microbial counts occurred.

During the year, after each harvest, each incoming flour batch presents a high variability in terms of rheological parameters, which depends on the wheat varieties, either employed as pure or in mixtures and on factors such as weather conditions and agronomic techniques, all of which play a different role in determining wheat performance (Bordes *et al.* 2008; Carcea *et al.* 2006; Flaete *et al.* 2005; Tea et al. 2007).

A variety of methods for the monitoring of gelatinization of starch are available, including different microscopic, thermoanalytical, enzymatic and rheological methods (Bao and Bergman, 2004). The recent trends in starch research have indicated the utilization of combined measurement techniques as reported by Li *et al*. (2013) who coupled hot-stage light microscopy and differential scanning calorimetry (DSC) to study the dynamic changes of starch during gelatinization process. Rheological methods are based on the measurement of viscosity changes during heating and shearing of starch slurries (Gunaratne and Corke, 2004). For this purpose, different instruments are available including Brabender Visco Amylograph (BVA) and Micro

Visco Amylograph (MVA), Rapid Visco Analyzer (RVA), Ottawa starch viscometer (Voisey et al. 1977) and viscometer (Lee *et al.* 1995).

Wheat flour, with 75ï 80 % of starch content on a dry weight basis, represents significant source of starch for the majority of population. The functional properties of starch such as gelatinization, gelation and viscosity are of great importance because they affect processing flour quality and final quality of baked products (Morris, 2004). The Brabender Amylograph (BA) has been in extensive use in wheat and/or flour research to assess starch gelatinization and pasting behavior primarily due to easy performance, standardized procedure and good correlation with final product quality.

Pojic *et al.* (2013) optimized the fundamental rheological method for determination of the gelatinization properties of wheat flour that correspondents to the standard widely accepted empirical rheological methodð Amylograph method and compared them in order to determine whether they can be interchangeable depending on different analytical needs. The obtained results have shown that the application of fundamental rheometric procedure for determination of pasting properties of wheat flour provides reliable determination of the gelatinization properties of wheat flour. Moreover, substantial advantages of fundamental rheometric method over the empirical one were identified including smaller sample size, ability to set the desirable heating and shear rate, shorter test duration and better precision.

PASTA QUALITY

Good cooking quality in pasta from durum wheat semolina is commonly characterized by high firmness, absence of stickiness and low cooking loss, characteristics that express high

cooking and overcooking tolerance (DôEgidio *et al*. 1990). The extent of protein coagulation and starch gelatinization phenomena, and consequently the overall cooking quality of the final product, is greatly affected not only by the native properties of semolina, especially protein quantity and quality (DôEgidio *et al*. 1990; Feillet and Dexter 1996), but also by the temperatureï moisture conditions applied during drying (De Noni and Pagani 2010). Marti *et al*. (2013) verified the suitability of two empirical and simple rheological approaches, as the tests based on MVAG and GPT (Brabender GmbH and Co. KG, Duisburg, Germany), to detect the starch and protein arrangements in dried pasta, which can differ according to durum wheat variety and pasta making conditions, and therefore, give information suitable for predicting pasta cooking behavior.

Good quality semolina (from sample A) exhibited a high pasting temperature, low hot viscosity, and high and earlier protein aggregation properties. In regard to pasta, when dried at a low temperature, spaghetti from sample A showed lower cooking loss than pasta from poor quality semolina (B), which is probably related to the low starch swelling and a strong network. The use of high temperature (HT) drying cycle lowered the differences in cooking quality and starch and protein properties related to the raw-materials features.

Chemometrics-multivariate analysis

Recently (Li Vigni *et al.* 2009) employed multivariate analysis of flour rheological properties in order to evaluate the performance in a more complete perspective, particularly from a multivariate control chart (Kourti, 2009) point of view, as already applied in other industrial fields (Camacho *et al.* 2008; Karoui and De Baerdemaeker, 2007). Li Vigni *et al.* (2013)

evaluated the influence of flour batches properties on bread quality, considering an industrial bread making process. In particular, flour composition in terms of protein fractions (gliadins, glutenins) has been determined by means of RP-HPLC, to assess the inter- and intra-batch variability of flour mixtures deliveries at a baking plant. Multivariate data analysis allowed evaluation of correlation between flour protein composition and technological properties. A great variability within different deliveries of a same flour batch emerged, as well as a considerable seasonal variability. Correlation models among protein sub-fractions, technological properties and bread quality are difficult to establish; however, the role of the protein profile on flour behaviour in bread making could be highlighted.

DETERMINATION OF DOUGH PROPERTIES

A creep recovery test can be applied In order to study the viscoelastic properties of dough and determine the reaction of a sample to a constant stress through recording the value of its strain as the function of time (Wang and Sun 2002).

Bread crumb with acceptable characteristics requires a balance between the viscous and elastic properties of dough. Though dough must be adequately viscous to retain the carbon dioxide produced during proving, it must also be sufficiently elastic to allow the bubbles to expand and agglomerate with other bubbles.

Creep recovery tests can then be related to the final bread characteristics such as bread volume, crumb pore size distribution or staling (Onyango *et al.* 2009; Van Bockstaele *et al*. 2011), and still an optimal balance between the viscous and elastic properties of dough is required.

Dough rheology tests estimate parameters such as stability, mixing time, extensibility, resistance to extension, tolerance to breakdown, strength, and water absorption. Baking performance is assessed by measuring traits such as loaf volume, texture and structure.

PRODUCTION OF PASTRY PRODUCTS

The most important processes in the production of pastry products derived from cereals are the following.

Weighing / Mixing of flours

Flour, water and yeasts are weighed to form a paste and become a homogenous mixture. At this step, the personnel should comply with the GMP (Good Manufacturing Practice) and GHP (Good Hygiene Practice).

Kneading

During flour mixing, a fine dispersion of bubble air cells must be formed within the dough volume. The dough must contain active yeasts and adequate nutritional substrate for the yeasts and the production of carbon dioxide, during the alcoholic fermentation, so that the bubbles are inflated. Furthermore, the dough must be properly produced for inflation purposes. In the long duration method, kneading lasts for 3 hours, while using the Chorleywood Bread Process (CBP) method the kneading process lasts for 2-4 min with the aid of a mixer (11Wh/kg). In this way during mixing heat is released resulting in a final dough temperature of 30°C. The materials before mixing should be of low temperature. After kneading, the dough is cut, put in patterns and finally molded. The first inflation takes place at 30°C for 10 min. Once inflation is over, the dough is molded again and placed in the forms (Varzakas and Arvanitoyannis, 2007).

Extruded wheat flours

Extruded wheat flours, due to their increased water absorption capacity, constitute an opportunity to increase bread output in bakery production. However extrusion may modify dough and bread characteristics. Martinez *et al*. (2013) investigated the effect of the substitution of 5% of the wheat flour by extruded wheat flour (produced with different time-temperature extrusion treatments) on dough mixing, handling and fermentation behaviour and bread volume,

shape, texture and colour. The Rapid Visco Analyzer (RVA) curves indicate that extrusion intensity increases with increasing temperature or water content. Water absorption capacity rises with increasing treatment intensity, but dough stability tends to decrease. Adding extruded flours decreases dough extensibility but increases tenacity and gas production. Differences in dough structure were observed on photomicrography, though there were no clear differences in bread quality. These results indicate that it is possible to obtain adequate dough and bread characteristics using dough with 5% extruded wheat flour.

Extrusion produces gelatinization of starch and increased damaged starch content, together with a reduction in lipid oxidation due to enzyme inactivation, an increase in soluble fibre and a reduction in thermolabile vitamins, antinutritional factors and microbial load (Camire *et al.* 1990). Extrusion also causes higher levels of mechanical damage in starch than traditional cooking methods (Wolf, 2010). Extruded wheat flours may therefore be an interesting alternative to pregelatinized starch and hydrocolloids to increase bread output in the bakery manufacturing process.

Few studies have investigated the use of extruded flours in bread-making and they are limited to the addition of these flours into non-wheat doughs or into doughs with a high content of nonwheat flours such as maize (Curic *et al.* 2009), barley (Gill *et al.* 2002) or rice (Sanchez *et al.* 2008) flours in order to make up for gluten deficiency.

Sodium chloride

Sodium chloride (NaCl), a major source of sodium in manufactured foods, is added to cereal based food not only to enhance the sensory properties, but also for its impact on the

functional properties of cereal constituents (e.g. proteins and starch, etc.) to allow appropriate processing handling and final textural characteristics (Miller and Hoseney, 2008).

Many studies have shown that sodium chloride increases the mixing tolerance of wheat flour dough, extends the dough development time and increases the dough resistance, elasticity and extensibility (Uthayakumaran *et al.* 2011). Part of this dough strengthening effect is due to the decrease in the water absorption of the flour. Beck *et al.* (2012) showed that reduction of NaCl in dough changed the gluten protein network structure from elongated protein strands to less connected protein particles. The difference in gluten microstructure in the presence or absence of NaCl is likely to be associated with how gluten proteins are hydrated at the very initial stages of mixing during which the presence of NaCl could reduce the surface charge of gluten proteins, thus its ability to interact with water molecules. Although it has been suggested that the presence of NaCl delays gluten hydration, there has been no direct evidence to confirm this hypothesis Sodium chloride (NaCl) is an essential ingredient to control the functional properties of wheat dough and bread quality.

McCann and Day (2013) investigated the effect of NaCl at 0, 1 and 2%, (w/w, flour base) on the gluten network formation during dough development, the dough rheology, and the baking characteristics of two commercial flours containing different levels of protein (9.0 and 13.5%) and with different gluten into-gliadin ratios. Examination of the dough structure by confocal microscopy at different stages of mixing show that the gluten network formation was delayed and the formation of elongated fibril protein structure at the end of dough development when NaCl was used. The fibril structure of protein influenced the dough strength, as determined by strain hardening coefficient and hardening index obtained from the large deformation extension

measurements. NaCl had a greater effect on enhancing the strength of dough prepared from the low protein flour compared to those from the high protein flour. The effect of NaCl on loaf volume and crumb structure of bread followed a similar trend. These results indicated that the effect of NaCl on dough strength and bread quality may be partially compensated by choosing flour with an appropriate amount and quality of gluten protein.

With current health care costs accounting for greater than 15% of the national expenditure, governments are seeking innovative cost-limiting strategies. Medical nutrition therapy (MNT) has proven to be an efficient cost minimising tool whilst concurrently ameliorating the patient's quality of life. In the MNT approach, the incorporation of foodomics technologies in medical foods has a pivotal role regarding quality, safety, nutrition and health (Zannini *et al.* 2013). These MNTs are defined as specially processed or formulated foods that are used for the dietary management of patients. Amongst the medical foods, low-protein/protein-free (LP/PF) foods have been shown to improve the physical manifestation of metabolic disorders in patients with amino acid or protein-related diseases, such as Phenylketonuria, Tyrosinaemia type I, aswell as chronic kidney, and coeliac.

Most of the cereal-based LP/PF foods currently marketed are a blend of refined or chemically-based food ingredients with unpalatable, frequently artificial flavours, having excessive sweetness to mask the chemical tasting ingredients (drug-like approach). However, the adoption of an alternative to convention, such as a food-like approach to developing medical foods, is a surprisingly complex process. This is specifically true when the technological aspects of LP/PF foods and, in particular, protein-free cereal foods are considered. The primary processing issues arise when trying to replace gluten in baked cereal products. This presents a

significant technological challenge, as gluten is an essential structural network-building protein necessary for formulating high-quality baked goods. Additional considerations such as physical/chemical compatibility, product shelf life, appearance, and palatability determine the success and potential for commercialisation of these therapeutic foods. Zannini *et a*l. (2013) addressed the suitable food technology strategies, in particular the foodomics research areas comprising genomics, proteomics, metabolomics and materiomics, for developing LP/PF cereal foods able to overcome the significant limitations of a food-like approach.

STALING OF CEREAL-BASED PRODUCTS

Staling is used to describe the deleterious chemical and physical changes that take place during storage of bakery products and is mainly related with an increase in crumb firmness and a parallel loss in product freshness. These changes are related to chemical or physicochemical phenomena and not to microbiological spoilage according to (Guy 1983) and are linked with a loss of eating quality by the consumers due to color, flavor, or texture deterioration.

A predominant role has been assigned to starch retrogradation, as starch is a major component of the system, which involves the progressive association of gelatinized starch segments into a more ordered structure (Zobel and Kulp 1996). Amylopectin retrogradation contributes significantly to staling or undesirable firming of bread and other starch-based products, whereas amylose plays a less important role in staling. Tolerance to staling determines the quality and shelf life of industrial cakes. Unlike bread staling phenomena, hardening in cakes, which are complex systems where several ingredients interact with each other affecting their texture, has not been so extensively studied (Gelinas *et al.* 1999). Cake staling is generally

referred as a complicated process, including loss and redistribution of moisture along with starch retrogradation, that results in flavour and tenderness loss and in mouth texture deterioration (Gomez *et al.* 2010). All these changes contribute to diminish consumer acceptability. Staling is much slower in cakes than in breads that may be partly attributed to the higher fat and lower flour content of cakes and moreover to the lower starch level that is expected to delay the staling of cake (Gelinas *et al.* 1999).

The staling of cakes enriched with untreated brans and endoxylanase-treated brans was evaluated by monitoring the changes in physicochemical, thermal, and sensorial properties of cakes during 7-d storage (Lebesi and Tzia, 2011). Oat and rice bran were treated with different levels (0, 70, and 700 ppm) of an endoxylanase enzyme and added to cakes on 30% flour weight basis. Moisture losses, water activity, crumb firmness, starch retrogradation, and sensorial characteristics were used as staling indicators. Avrami-type equations were efficiently used for modeling the starch retrogradation kinetics, while linear models most adequately described crumb firming kinetics. Cake staling induced an increase in crumb firmness and enthalpy of amylopectin retrogradation, and a decrease in crumb moisture and sensory quality and acceptability scores of cakes. Oat bran-containing cakes better maintained their characteristics compared to the ones containing rice bran along the 7-d storage. Endoxylanase treatment of brans delayed the changes naturally induced during staling in crumb moisture content, amylopectin retrogradation enthalpy, and crumb firmness in the respective cakes. Deterioration of the sensorial characteristics was slower for the cakes containing endoxylanase-treated brans, as well. The level of endoxylanase treatment did not differentiate significantly ($P < 0.05$) any of

the staling indicators. Overall, this study demonstrated that addition of endoxylanase-treated brans can result in cakes with improved nutritional characteristics and increased shelf life.

SAFETY ASPECTS IN CEREAL-BASED PRODUCTS (with special focus on wheat)

Mycotoxins

Mycotoxins in food and animal feed, is a major problem concerning the safety of the animal stock as well as the public health. It is well known that mycotoxins are responsible for carcinogenic effects in animals and humans. Mycotoxins are toxic secondary metabolites produced by certain strains of *A. flavus* and *A. parasiticus*. Mycotoxins in foods (cereals, coffee, cocoa, spices, dried fruit, dried beans and apples) may come from the field or warehouses. The need for mycotoxins control has led to the development of specific analytical methods. If storage conditions are not well after harvest, aflatoxigenic fungi invade the grains and cause serious damage producing aflatoxins. Some of the fungicides are effective in preventing growth of *A. flavus* in storage especially as a fumigant there are consumer concerns regarding the risks associated with the use of fungicides.

Mycotoxins can be produced on a wide range of cereals, particularly on barley, wheat, oat, corn, rice. Grain contamination and damage may occur in the field during kernel maturation, harvesting, transportation and storage, if high moisture is present. Mycotoxins produced by field fungi *Fusarium*: trichothecenes - nivalenol (NIV), deoxynivalenol (DON) and its derivatives, T-2 and HT-2 toxins (T-2; HT-2); zearalenone (ZEA), moniliformin, fumonisins were detected in

some samples of wheat, barley, rice, corn, oat from different countries (Campbell et al., 2000; Lauren et al., 1991; Malachova et al., 2010; Tanaka et al., 1988; Scott, 1990; Tutelyan et al., 1990). Mycotoxins of storage fungi *Penicillium* and *Aspergillus:* aflatoxins (Afl), ochratoxin A (OTA), citrinin and other - were detected in part of samples of all cereals (Sweeney et al., 2000; Trigo-Stochli et al., 1995; Weddeling et al., 1994**)** and there would appear to be a significant risk of their formation in grain which is stored improperly or for extended period of time.

Detoxification of aflatoxins offers a safer approach. There have been reported several strategies for aflatoxins detoxification such as by physical, chemical and biological means. Chemical includes ammoniation, treatment with formaldehyde and calcium hydroxide, ozonization, exposure to chlorine gas and hydrogen peroxide. Microbial detoxification includes *Flavobacterium aurantiacum*, *Mucor* spp., *Rhizopus* spp., *Corynebacterium* and nontoxigenic strains of *A. flavus* and *A. parasiticus*. Physical detoxification includes hydrated sodium calcium aluminosilicate (Varzakas *et al.* 2012).

Deoxynivalenol (DON, or vomitoxin), a trichothecene group of mycotoxin is the most prevalent toxin worldwide in crops used for food and feed consumption (Larsen, *et al.* 2004). It is produced by *Fusarium graminearum* and *Fusarium culmorum* group of fungi. DON frequently occurs in wheat, maize, barley, oats, and rye as well as processed grains malt, beer and bread.

The occurrence, frequency, and implications of DON entering the food chain through cereal grain have gained global attention, especially in the last decade with frequent outbreaks of Fusarium Head blight and Fusarium Ear rot in many cereal-growing regions (McMullen, 1997). Thus considering toxicity of DON European Commission (2006) (E.U) has introduced maximum

permissible limit 1250 ε g/kg for DON in unprocessed cereals other than durum wheat, oats and maize, 1750 ε g/kg in unprocessed durum wheat and oats, 750 ε g/kg in finished products (cereals intended for direct human consumption, cereal flour, bran and germ as end product), 500 ε g/kg bread (including small bakery wares), pastries, biscuits, cereal snacks and breakfast cereals and 200 ε g/kg for processed cereal-based foods and baby foods for infants and young children, to reduce the risk to the consumer.

The occurrence of DON in hundred samples of wheat, maize and barley collected from different districts of Uttar Pradesh, India was examined by Mishra *et al*. (2013). DON was detected in 30% samples out of which 7% samples exceeded the FSSR (Food Safety and Standard Regulation, India) limit (1 mg/kg). The contamination levels ranged from 0.01 mg/kg to 4.73 mg/kg. Of all the hundred cereal samples analyzed by HPLC, 19 positive samples (within the limit of quantification LOQ of 0.043 mg/kg) were further quantified by High Pressure Thin Liquid Chromatography (HPTLC), which showed comparable results suggesting that HPTLC is an equally reliable and cost effective method. Validation of DON in samples was performed by LC-MS analysis. Based on results of monitoring and the average actual consumption of wheat in India, the 90th percentile value of estimated daily intake (EDI) of DON was found to be 7.72 ε g DON/kg body weight which exceeded the Provisional Maximum Tolerable Daily Intake (PMTDI 1 ε g DON/kg-bw) proposed by JECFA by 7.7 folds there by suggesting the possibility of DON exposure to humans. Since DON levels have been set for wheat only there is a need to formulate regulatory standards for other cereals so as to reduce the exposure risk to DON.

Several recently emerged *Fusarium* toxins, represented by enniatins (ENNs), beauvericin (BEA), fusaproliferin (FUSA) and moniliformin (MON) have appeared recently. ENs and BEA

mycotoxins are produced by different *Fusarium* species such as *Fusarium verticillioides, Fusarium proliferatum, Fusarium subglutinans, Fusarium oxysporum, Fusarium poae* and *Fusarium avenaceum*. These molds colonise many important food commodities and prevail in warmer and temperate areas of central and south-eastern Europe. Its accumulation in grains can cause a potential risk to human and animal health, if they are consumed via feed or food products (Pestka, 2010).

In the recent years, BEA and ENs have been described as frequent contaminants in grains, 50ï 90% for wheat, corn and barley, contaminants in grains, potatoes and apples used as food and animal feed in several countries (Jestoi, 2008; Sorensen et al. 2009). High contamination levels have been recently reported, up to 10ï 500 mg/kg, for the sum of BEA and ENs in wheat, barley and corn from southern, central and northern Europe (Jestoi, 2008). In a study reported by Juan et al. (2013), 48 multicereal baby foods samples including 25 of pasta and 23 of multicereal baby foods from supermarkets of Campania region (Italy) were analysed for evaluating the presence of beauvericin (BEA) and enniatins (ENs) A, A1, B, B1 and B4. Subsequently to evaluate the risk exposure of Italian population and infant population over the consumption of pasta or multicereal baby food, was, respectively, evaluated.

For the above mentioned evaluation, a method developed in their laboratory by liquid chromatography tandem mass spectrometry was used. A liquid phase dispersion procedure was optimised for the simultaneous extraction of BEA and the five ENs from multicereal baby food samples and pasta. The main parameters affecting extraction yield and selectivity, extraction solvent were evaluated.

Analytical results showed that the occurrence of BEA, ENA, ENA1, ENB, ENB1 and ENB4 in analysed pasta and multicereal baby food samples were below 68% and 74%, respectively. ENB was the mycotoxin most found and levels in pasta and baby food ranged from <limit of quantification (LQ) to 106 and from <LQ to 1100 ε g/kg, respectively. It was observed a high incidence (70.3%) and high contamination levels (<1100 ε g/kg) of these mycotoxins in multicereal baby food and its intakes could represent a risk for the infant population (estimated daily intake <7.23 ε g/kg bw/day).

Malachova *et al*. (2011), found altogether 23 mycotoxins representing the following four groups: (i) trichothecenes and zearalenone (ZEA); (ii) ENNs and BEA; (iii) ergot alkaloids; and (iv) alternaria toxins, were monitored in flours and some other cereal-based products, e.g., bakery products, breakfast cereals, and snacks, collected from the Czech market. Common trichothecenes B and four ENNs (A, A1, B and B1) were present in samples at relatively high levels. While the frequent presence of DON together with its conjugate DON-3-glucoside (DON-3-Glc) was in line with their expectation, high occurrence of at least one of four target ENNs practically in all of the 116 examined samples was rather surprising. The most abundant was ENN A, which was detected in 97% of samples (concentration range 20ï 2532 ε g/kg), and followed by ENN B with an incidence in 91% of samples (concentration range 13ï 941 ε g/kg).

Vaclavikova *et al*. (2013) reported on the fate of these *Fusarium* mycotoxins within malting, brewing, milling and baking, when employed for the processing of contaminated barley and wheat. Besides enniatins A, A1, B and B1, also deoxynivalenol and its conjugated form (deoxynivalenol-3-glucoside) were determined in almost all tested cereal-based samples. Significant decline of enniatins occurred within all technologies, with the largest drop in their

concentrations observed in the brewing process. While enniatins were not detectable in final beers, they were almost quantitatively transferred to spent grains, probably because of their limited water solubility. Regarding bread baking, levels of enniatins decreased down to 30% of their concentration in the initial flour used for baking. In this case, degradation at higher temperatures might be assumed.

Fusarium mycotoxins occur worldwide in foods such as cereals and animal forages, leading to acute and chronic exposures in human and animals. Intestinal epithelial cells (IECs) are an important first target site for these dietary toxins. Wan *et al*. (2013) investigated the cytotoxicity of four common *Fusarium* mycotoxins, DON, nivalenol (NIV), ZEA and fumonisin B1 (FB1) on a normal porcine jejunal epithelial cell line, IPEC-J2. A dose response relationship between individual mycotoxins and cell viability Methyl Thiazol Tetrazolium (MTT assay) was initially investigated, and subsequently cytotoxic and non-cytotoxic concentrations were selected to investigate combinations of two, three and all four of the mycotoxins. For individual mycotoxins, a dose response was observed with cell viability, such that the potency ranking was NIV > DON > ZEA > FB1. At cytotoxic doses of individual mycotoxins, all mixtures gave reduced cell viability compared to control. At noncytotoxic concentrations of individual mycotoxins, all mixtures were cytotoxic with DON-NIV, DON-ZEA, DON-NIV-FB1, DON-ZEA-FB1, NIV-ZEA-FB1 and all four mixed causing the greatest loss of cell viability. The latter observation in particular raises concerns over safety margins based on single toxin species, and suggests that the effects of multiple complex mixtures need to be better understood to assess health risks.

Hu *et al*. (2013) described a proposed method for convenient and sensitive detection of *Fusarium* pathogens that uses the fusion of single-chain variable fragment (scFv) and alkaline phosphatase (AP). A highly reactive scFv antibody specific to soluble cell wall-bound proteins (SCWPs) of *F. verticillioides* was selected from an immunized chicken phagemid library by phage display. The antibody was verified to bind on the surface of ungerminated conidiospores and mycelia of *F. verticillioides*.

The scFvï AP fusion was constructed, and soluble expression in bacteria was confirmed. Both the antibody properties and enzymatic activity were retained, and the antigen-binding capacity of the fusion was enhanced by the addition of a linker. Surface plasmon resonance measurements confirmed that the fusion displayed 4-fold higher affinity compared with the fusionôs parental scFv antibody. Immunoblot analyses showed that the fusion had good binding capacity to the components from SCWPs of *F. verticillioides,* and enzyme-linked immunosorbent assays revealed that the detection limit of the fungus was below 10^{-2} ε g mL^{-1}, superior to the scFv antibody. The fusion protein was able to detect fungal concentrations as low as 10^{-3} mg g^{-1} of maize grains in both naturally and artificially contaminated samples. Thus, the fusion can be applied in rapid and simple diagnosis of *Fusarium* contamination in field and stored grain or in food.

A quantitative dietary exposure assessment of mycotoxins and their masked forms was conducted by De Boevre *et al*. (2013) on a national representative sample of the Belgian population using the contamination data of cereal-based foods. Cereal-based food products (n = 174) were analysed for the occurrence of DEA, 3-acetyldeoxynivalenol, 15-acetyldeoxynivalenol, ZEA, Ŭ-zearalenol, ɓ-zearalenol, T-2-toxin, HT-2-toxin, and their

respective masked forms, including, deoxynivalenol-3-glucoside, zearalenone-4-glucoside, Ŭ-zearalenol-4-glucoside, ɓ-zearalenol-4-glucoside and zearalenone-4-sulfate. Fibre-enriched bread, bran-enriched bread, breakfast cereals, popcorn and oatmeal were collected in Belgian supermarkets according to a structured sampling plan and analysed during the period from April 2010 to October 2011. The habitual intake of these food groups was estimated from a national representative food intake survey. According to a probabilistic exposure analysis, the mean (and P95) mycotoxin intake for the sum of the deoxynivalenol-equivalents, zearalenone-equivalents, and the sum of HT-2-and T-2-toxin for all cereal-based foods was 0.1162 (0.4047, P95), 0.0447 (0.1568, P95) and 0.0258 (0.0924, P95) ε g kg^{-1} body weight day^{-1}, respectively.

These values were below the tolerable daily intake (TDI) levels for DON, ZEA and the sum of T-2 and HT-2 toxin (1.0, 0.25 and 0.1 ε g kg^{-1} body weight day^{-1}, respectively). The absolute level exceeding the TDI for all cereal-based foods was calculated, and recorded 0.85%, 2.75% and 4.11% of the Belgian population, respectively.

Han *et al.* (2013) performed quantitative assessment of risk associated with dietary intake of ochratoxin A (OTA) based on consumption habits of the representative adult inhabitants in Shanghai city of P. R. China. Firstly, a total of 400 food samples randomly collected from different locations of Shanghai were analyzed by the previously established isotope dilution LC-MS/MS method. Then, 265 participants of 70 males and 195 females as representative inhabitants were invited to answer the designed questionnaire about the quantity and frequency of foods including four major varieties of grapes, cereals, beans and dried fruits as well as their derived products. Finally, all data were simulated by the point evaluation and model evaluation for the risk assessment of OTA contamination. Results from the point evaluation indicated that

mean value of daily intake (DI) of OTA was 1.147 ng/kg body weight/day, which was lower than all the reference standards. However, DI value (8.566 ng/kg body weight/day) in the high percentile (97.5th) was obviously higher than the PTDI (5 ng/kg body weight/day) proposed by Scientific Committee on Food. Among the different groups of foods, OTA in cereals and derived products made the largest contribution to the potential healthy risk. The mean DI value and 97.5th percentile were 1.093 and 7.962 ng/kg body weight/day, respectively, indicating that more than 90% of the risk was due to the contamination of OTA in cereals and derived products. On the other hand, similar results were obtained by the Monte Carlo assessment model. Thus, from the currently available data and analyzed results on the adult inhabitants, regarding OTA contamination issues on food safety administration of Shanghai, there was no significant attention which should be paid on food consumption in Shanghai, besides cereals and derived products with very little possibility as the risk factors.

Lacina et al. (2012) addressed a current trend in chemical food safety control by an effort to integrate analyses of various groups of food contaminants/toxicants into a single, high-throughput method. The choice of optimal sample preparation step is one of the key conditions to achieve good performance characteristics. In this context, they investigated the possibility to expand the scope of the three multi-analyte extraction procedures employed earlier in other studies for rapid isolation of either pesticides or mycotoxins from plant matrices. Following procedures were tested: A ï aqueous acetonitrile extraction followed by partitionquick, easy, cheap, rugged and safe (QuEChERS-like method), B ï aqueous acetonitrile extraction, and C ï pure acetonitrile extraction. On the list of target analytes, we had 288 pesticides (including ątroublesomeô acidic, basic and base-sensitive compounds) together with 38 mycotoxins

(including all EU regulated ones and many ćemergingô toxins on the European Food Safety Authority (EFSA) list). The matrices selected for the experiments, apple baby food, wheat flour, spices and sunflower seeds, represented various composition categories in terms of moisture, fat and extractable compounds (e.g. pigments and essential oils) content. In preliminary experiments, acceptable recoveries (70ï 120%) for most of analytes were obtained by the analysis of spiked matrices, regardless which extraction procedure was used. However, when analysing dry samples with incurred pesticide residues/mycotoxins, the method C did not enable efficient extraction of some common contaminants. Procedure A, thanks to a higher matrix equivalent compared to the method B and relatively less pronounced matrix effects, enabled lower quantification limits for all analyte/matrix combinations, with the exception of polar mycotoxins and/or pesticides. Higher recoveries for the latter group of analytes could be achieved by the method B; on the other hand, extraction efficiency of non-polar pesticides from fatty matrix was rather poor by this method.

The selected matrices were: (i) apple baby food (high moisture matrix); (ii) wheat flour (low moisture, high content of starch); (iii) paprika and black pepper (low moisture, high content of extractable compounds); (iv) sunflower seeds (low moisture, high content of lipids). Except the experiments on spiked matrices, methods performance on incurred pesticide residues and mycotoxins were evaluated by means of the analysis of certified reference materials and samples obtained within the inter-laboratory comparisons. The extracts prepared by different extraction methods were analysed by ultra-high performance liquid chromatographyï electrospray ionisation-tandem mass spectrometry (UHPLCï ESIMS/MS).

The levels of five mycotoxins, for which the Maximum Allowable Limits (MAL) in cereals have been regulated in EU (2006): DON, T-2, ZEA, Afl and OTA- were determined with commercial direct competitive ELISA test kits RIDASCREEN FAST (R-Biopharm AG, Germany) (Table 1). (Test kit RIDASCREEN FAST Aflatoxin ï for the quantitative analysis of sum of aflatoxins B_1, B_2, G_1, G_2.

Near Infrared (NIR)

Near-infrared (NIR) hyperspectral imaging has proved its suitability for quality and safety control in the cereal sector by allowing spectroscopic images to be collected at single-kernel level, which is of great interest to cereal control laboratories. Contaminants in cereals include, inter alia, impurities such as straw, grains from other crops, and insects, as well as undesirable substances such as ergot (sclerotium of *Claviceps purpurea*). For the cereal sector, the presence of ergot creates a high toxicity risk for animals and humans because of its alkaloid content. A study was undertaken by Vermeulen *et al*. (2013), in which a complete procedure for detecting ergot bodies in cereals was developed, based on their NIR spectral characteristics. These were used to build relevant decision rules based on chemometric tools and on the morphological information obtained from the NIR images. The study sought to transfer this procedure from a pilot online NIR hyperspectral imaging system at laboratory level to a NIR hyperspectral imaging system at industrial level and to validate the latter. All the analyses performed showed that the results obtained using both NIR hyperspectral imaging cameras were quite stable and repeatable. In addition, a correlation higher than 0.94 was obtained between the predicted values obtained by NIR hyperspectral imaging and those supplied by the stereo-

microscopic method which is the reference method. The validation of the transferred protocol on blind samples showed that the method could identify and quantify ergot contamination, demonstrating the transferability of the method. These results were obtained on samples with an ergot concentration of 0.02 % which is less than the EC limit for cereals (intervention grains) destined for humans fixed at 0.05 %.

Since the late 1970s, near infrared (NIR) spectroscopy coupled with chemometrics has been successfully used to characterize cereal samples. Multivariate calibration on NIR spectra is now commonly used for routine analysis to determine protein, moisture, gluten, fiber content, and hardness in flours (Osborne and Fearn, 1986; Manley et al., 2002).

However, the medium infrared (MIR) region can be used to determine the composition of ground cereals with an accuracy equal to or better than that obtained by NIR.

Cocchi et al. (2004) studied different kinds of cereal flours submitted to various technological treatments and classified them on the basis of their mid-infrared spectra by pattern recognition techniques. Classification in the wavelet domain was achieved by using the wavelet packet transform for efficient pattern recognition (WPTER) algorithm, which allowed singling out the most discriminant spectral regions. Principal component analysis (PCA) on the selected features showed an effective clustering of the analyzed flours.

Satisfactory classification models were obtained both on training and test samples. Furthermore, mixtures of varying composition of the studied flours were distributed in the PCA space according to their composition.

In wheat, Near Infrared Reflectance Spectroscopy (NIRS) is frequently used by breeders to predict the chemical composition and properties of flour. Whole NIRS spectra provided a

useful tool for describing the global evolution of the chemical composition of the grain of French wheat.

Moreover, the compositional changes over a 200 year period in a collection of bread wheat accessions have been measured by Roussel et al. (2005). Roussel et al. (2005) used whole spectra obtained by Near Infrared Reflectance Spectroscopy (NIRS) to follow the evolution of four groups of wheat components (proteins, minerals, fatty acids and carbohydrates) in a set of 539 French bread wheat accessions released and cultivated during the last two centuries in France.

Cocchi et al. (2005) analysed various wheat flour samples by means of NIR spectroscopy, and the obtained spectra have been classified both by SIMCA applied to the signals subjected to different pretreatment methods, and by using a wavelet-based feature selection/classification algorithm, called WPTER. Acceptable results have been obtained for the classification of the two most different baking categories, which can be at least partially separated each other using only six variables (wavelet coefficients) derived from the NIR spectra.

Acrylamide

The European Funded Project BRAFO (benefitï risk analysis of foods) project was to develop a framework that allows quantitative comparison of human health risks and benefits of foods based on a common scale of measurement. This publication by Schütte et al. (2012) described the application of the BRAFO methodology to three different case studies: the formation of acrylamide (AA) in potato and cereal based products, the formation of

benzo(a)pyrene through smoking and grilling of meat and fish and the heat-treatment of milk. Reference, alternative scenario and target population represented the basic structure to test the tiers of the framework.

Various intervention methods intended to reduce AA in potato and cereal products were evaluated against the historical production methods. In conclusion the benefits of the AA-reducing measures were considered prevailing. AA has been selected as a case study because it is one of the best characterized heat-processing contaminants known in food. It is an animal carcinogen and while human epidemiological data is not fully conclusive, results from animal studies suggest this contaminant could impair health (Shipp *et al.* 2006; Klaunig, 2008; Becalski et al., 2003).

Acrylamide (AA) is an industrial chemical and a food contaminant which may be formed in foods, particularly carbohydrate-rich and protein-low plant commodities, during cooking, frying, baking or roasting at temperatures of 120 ºC or higher. Most foods made from cereals, potatoes and also coffee, and some other foods have been shown to contain AA. The potential risks from use of different AA reduction tools are: Increased Ca-intake (Ca-salt addition in potato products), increased Na-intake (raising agent replacement in bakery ware, NaCl addition in potato products), increased 3-monochloropropane-1,2-diol (3-MCPD) intake (pH reduction in bakery ware), increased fat intake (lowered frying temperature in potato products), some loss of asparagine (use of enzyme asparaginase in potato and cereal products). AA-reducing actions should be applied as long as the adverse side effects are recognized and minimized to the extent possible (Schütte *et al.* 2012).

The risks of acrylamide to health and its toxic properties (neurotoxicity, genotoxicity, carcinogenicity and reproductive toxicity) were demonstrated by the Scientific Committee on Toxicity, Ecotoxicity and the Environment in 2001 and IARC (1994). Potato and bakery products account for around 50% and 20% of human exposure to acrylamide, respectively.

Factors affecting acrylamide formation and degradation in foods are acrylamide precursors such as free amino acids (mainly asparagine), reducing sugars and processing conditions (i.e. baking time and temperature, moisture content and matrix of product) (Keramat et al. 2011).

Direct consumer exposure to acrylamide may result from ingestion of high-carbohydrate foods such as potato crisps and chips, roasted cereals, and breads. The highest levels have been detected in the crust of the bread, whereas the crumb contains almost no acrylamide. One exception is crisp bread which contains considerable amounts of acrylamide.

Curtis et al. (2010) studied acrylamide precursors (free amino acid and sugar concentrations) in rye varieties and showed free asparagine concentration to be the main determinant of acrylamide formation in heated rye flour, as it is in wheat.

Hamlet et al. (2008) showed that in cooked flours and doughs (mainly rye and wheat), asparagine was the key determinant of acrylamide generation. They found that in biscuit and rye flours, levels of asparagine were correlated with fructose and glucose, so selection based on low fructose and glucose contents, and hence low asparagine, could be beneficial in reducing acrylamide in products (e.g. crackers and crisp breads) that have no added sugars.

Conclusions & future outlook

Safety and quality aspects of cereals, and most specifically wheat, are described in this chapter. Moreover, wheat quality aspects are adequately addressed since they are used to characterize dough properties and baking quality. Determination of dough properties is also mentioned. Quality control of cereals is described including chemometrics-multivariate analysis. The manufacturing of pastry products is also described here. Finally, safety aspects of cereal-based products focus on mycotoxins, acrylamide, and NIR methodology.

Moreover, the species composition of a cereal-based food is a key factor in determining the quality and safety of the final product.

In this work we have seen the link between quality, and more specifically organoleptic quality (appearance, texture, taste, freshness), and safety of cereal products with strong emphasis on wheat flour.

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Table 1 Maximum allowable limits of mycotoxins in cereals for food in EU and characteristics of RIDASCREEN FAST method.

Mycotoxins	Maximum allowable levels, $\varepsilon g \cdot kg^{-1}$ (ppb) (grain for food)		RIDASCREEN FAST (R-Biopharm)		
	Abbreviations	EU (2006)	Limit of detection (LOD), ppb	Limit of quantification (LOQ), ppb	Measuring range, ppb
Deoxynivalenol	(DON)	1250 (unprocessed cereals other than durum wheat, oats and maize)	200	200	200-6000
T-2ï toxin	(T-2)	100	<20	50	50-400
Zearalenone	(ZEA)	100 (unprocessed cereals)	17-41	50	50-400
Aflatoxins	Afl.	2.0 (Afl_1) 4.0 (Afl sum)	<1.7 (Afl sum)	5 (Afl sum)	1.7-45(Afl sum)
Ochratoxin A	(OTA)	5.0 barley 3.0 malt	5	5	5-40

