Received: 2 April 2021 | Revised: 17 May 2021 | Accepted: 28 May 2021

DOI: 10.1002/cche.10458

RESEARCH ARTICLE

# Content of minerals and deoxynivalenol in the air-classified fractions of durum wheat

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## Abstract

**Background and objectives:** Durum wheat (*Triticum durum* Desf.), such as other cereals, contains several interesting bioactive compounds mostly found within the coating structure of the kernel; also, these structures included in the bran fractions, contain the highest concentration of both minerals and organic contaminants (mycotoxins). The purpose of this project was to employ the micronization and air-classification technology to obtain fewer refined milling fractions with an adequate good quality in regard to safety and nutritional aspects to manufacture end products (e.g., pasta).

**Findings:** The results have identified the milling fraction as the best compromise among satisfactory technological traits, high decrease of cadmium (−83%) and lead (−59%) in comparison to the whole grain, high content of iron (+37%), and the maintenance of useful elements (calcium, potassium, and magnesium). A significant decrease of the deoxynivalenol (−16%) content, as compared with the micronized sample, and a not significant increase (+19%), if compared with semolina, have occurred.

**Conclusions:** The air-classification process has been used as an appropriate tool to reach a good compromise between minerals and deoxynivalenol content in milling fractions.

**Significance and novelty:** The same process has proved to be a proper technology to produce high-quality mixtures suitable to obtain both healthier end products and better raw matter exploitation.

KEYWORDS

air-classification, deoxynivalenol, durum wheat, micronization, minerals

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Alessandro Cammerata and Rosita Marabottini are the main authors and the first to promote and conduct this research project.

## 1 | INTRODUCTION

Epidemiological studies have linked the consumption of the whole grain and derivatives to a reduced incidence of cardiovascular diseases, cancer, and diabetes (Aune et al., 2016; Călinoiu & Vodnar, 2018); all these health consequences have mainly been associated both with the antioxidant activity of phytochemicals, also contained within cereals, and the dietary fiber intake (Onipe et al., 2015; Ficco et al., 2018). Therefore, the consumption of rich-in-fiber food is commonly recommended as an important strategy a healthy diet is based upon (Ötles and Ozgoz, 2014; Probst et al., 2017; Stephen et al., 2017).

The maintenance of several bioactive compounds within the coating structures of the kernel of wheat is highly interesting with regard to the biological and nutritional properties: Indeed, several compounds (e.g., β-glucans, lignans, folates, fructans, phytosterols, polyphenols, and arabinoxylans) that ease health benefits (e.g., prebiotic, antioxidant, hypoglycemic, hypocholesterolemic) are mostly present in the whole grain (Giordano et al., 2016; Fu et al., 2017); nevertheless, the outer structures of the kernel end up in the milling waste products (i.e., bran, middlings). The identification of milling fractions suitable to be employed for the production of functional food has been enriched with beneficial components that can be achieved by using appropriate technologies during the initial phase in the milling process or through a focused mixture of the selected fractions. However, the beneficial bioactive compounds can be associated with the presence of minerals, some of whom are toxic elements, and of organic compounds such as mycotoxins. In more detail, the final content of several minerals within the milling products depends on both the type of the element and its distribution within the structures of the kernel. Concerning metals, cadmium (Cd) is uniformly distributed within the endosperm, unlike copper (Cu), zinc (Zn), and iron (Fe)—all of these can be easily found in the aleurone layer—whereas lead (Pb), manganese (Mn), and nickel (Ni) are mainly located in the outer teguments (Conti et al., 2000; Ficco et al., 2020; Cubadda et al., 2003). As far as the mycotoxin contamination is concerned, deoxynivalenol (DON) is the most widespread *Fusarium*-toxin in small grain cereals and constitutes the most relevant source of exposure to this type of mycotoxin for humans and animals. Deoxynivalenol (DON) belongs to the type B group of trichothecenes, which have been mainly discovered in cereal crops, whose toxic effects are of great concern for human health (Gauthier et al., 2013; Maresca, 2013; Pinton & Oswald, 2014). This form of mycotoxin is produced by toxic varieties (e.g., *F. graminearum* and *F. culmorum*), which colonize the kernel from its outer layer progressively establishing the main source of grain contamination by DON and its modified forms (Khaneghah et al., 2018; Freire and Sant'Ana, 2018). The estimated mean chronic dietary exposure for humans was over the TDI (1 μg/kg b.w.) concerning infants, toddlers and other children, and also at high exposure in adolescents and adults, and it represents a potential problem for people's health (European Food Safety Authority, 2017). Maximum tolerable limits have been set by European Commission for Cd, Pb, and DON in food products (EC Regulation 1126/2007; EC Regulation 1881/2006).

As a result of the traditional milling process, all the outer layer structures of the kernel form the so-called "by-products fractions" (e.g., bran, fine bran, fine middlings), where both inorganic and organic compounds tend to concentrate (Brera et al., 2013; Schaarschmidt & Fauhl-Hassek, 2018); on the contrary, although the decrease in semolina has resulted higher for nickel, it has been gradually less substantial for arsenic, cadmium, and lead (Cubadda et al., 2003). Therefore, in the case of the manufacturing of less refined end products a grain processing technology is needed in such a way to manage negative and positive aspects efficiently (Fares et al., 2010; Ficco et al., 2020). On the other hand, the use of the whole milled wheat as a consequence of the manufacturing process can have a negative impact on products in terms of technological and sensorial properties due to the high content of bran (Onipe et al., 2015): An innovative approach toward the employment of proper technological solutions and new milled mixtures with improved functional and healthy properties would result as making high-quality products in terms of taste, and they would be more attractive to end users.

To resort to modern technologies, such as debranning, micronization, and air-classification during the initial phase of the production process could reveal itself as an effective method to properly contain undesirable compounds within the milling products (Wang et al., 2013; Brera et al., 2019). For example, by removing a small part of the outer layers (3%–5%) through the debranning process, a 10%–20% decrease of Cd and Zn was observed in cereal products that reached 80% for Pb (Brüggermann and Kumpulainen, 1995); the fate of several detrimental components was assessed in durum wheat and a 11% and 24% decrease concerning several traces of toxic elements was achieved when debranning treatment was applied, respectively, for 30s and 60s (Cheli et al., 2010; Ficco et al., 2020). Furthermore, the employment of micronization and air-classification technologies during the early phase of durum wheat's manufacturing process might constitute an appropriate way to obtain final products enriched in bioactive compounds. (Ficco et al., 2018). The micronization consists of a milling process that transforms the initial kernels into a mixture of fine particles; the air-classification is an effective method to separate the particles of the micronized mixture making fine and coarse fractions. By many decades, this kind of wheat processing has been widely used in the wheat milling industry, both to better exploit raw matter and promote innovative end products. The application of by-products in the food industry results as an added value toward both industry and consumer: the industry benefits from economic incomes and the consumer from the excellent nutritional value of these materials with potential health claims (Stringfellow et al., 1977; Wang et al., 2013).

## 2 | MATERIALS AND METHODS

### 2.1 | Samples

Two grain samples (*Triticum durum* Desf. "Anco Marzio" and "Svevo") have been collected in different growing areas of Italy (Central regions, Sardinia and Sicily); according to representativeness criteria, one 8.0 kg grain sample of Anco Marzio has been divided in the following way: 3.0 kg have been submitted to the traditional roller milling plant (TMP) in a single proof as specified in Section 2.2 (EC Regulation 401/2006), while the remaining part has been further divided into three sub-samples (I, II, and III) and then reduced to a fine wholemeal employing a micronizer; each of these three micronized sub-samples has been then just made subjected to one of the three setting conditions of the air-classification treatment (220, 250, and 280), according to the rate of the airflow inlet within the air-classification plant (ACP). The main milling products derived from TMP and the three fractions from ACP all have collected and analyzed both for minerals and mycotoxin content (Figure 1). In a similar way, four grain samples ($n = 4$) belonging to cv. Svevo have been submitted to the micronization treatment followed by the air-classification process: It was confined to the setting conditions that were more effective to the aim of this project.

### 2.2 | Traditional roller milling plant process (TMP)

The 17% of the moisture content of the 3.0 kg sample (cv. Anco Marzio) was conditioned by adding water letting it stand 24 hr. Such a specific treatment was helpful to simplify both the undressing process of the kernel and the softening of the endosperm; therefore, it was required to improve the quality of the milling treatment through the use of the traditional roller milling plant (Bühler, model MLU 202, Uzwil, Switzerland). The main milling products have collected afterward: semolina, the squandering of semolina due to the use of the experimental system (NAMAD Impianti, Rome, Italy) equipped with some varieties of sieve (38GG, 40GG and 44GG), fractions of bran (both coarse and refined bran), and fine middlings—the content of ash has been analyzed by the use of the UNI-ISO 2,171 method (two repetitions minimum).

### 2.3 | Air-classification plant process (ACP)

The previously mentioned three sub-samples (I, II, and III) of cv. Anco Marzio—whose weight was 1.0, 3.0, and 1.0 kg, respectively—have been subjected to a micronization procedure by using a milling pilot plant in the laboratory (mod. "Pulverisette," Fritsch, Kitzingen, Germany), helpful both for small and medium amounts of grain; the micronizer (the size of the sieve was set at 0.7 mm), which belonged to the mill cutting procedures, has been equipped with a rotor (ø 110 mm) and an engine power (2,800 revolutions per minute) capable of achieving the operating conditions (18,000 revolutions/minute): The heating has been prevented due to preset operative appropriate conditions. Indeed, with the same size setting conditions (0.7 mm), this system has been able to ensure results comparable to technological methods that are opportune for high volumes of raw matter (data not available). The micronization phase did not require a preventive conditioning of grains: Therefore, the aforesaid sub-samples have been submitted to an integrated air-classifying system (turbo-separator unit, SX-LAB model, Separ Micro System, Flero, BS, Italy), extremely adequate to size a specific setting limit up (Ø ≤ 1.5 mm). The functioning criteria of the air-classifying plant were based on the consequences among opposite forces, air-traction and centrifugal forces, by the use of

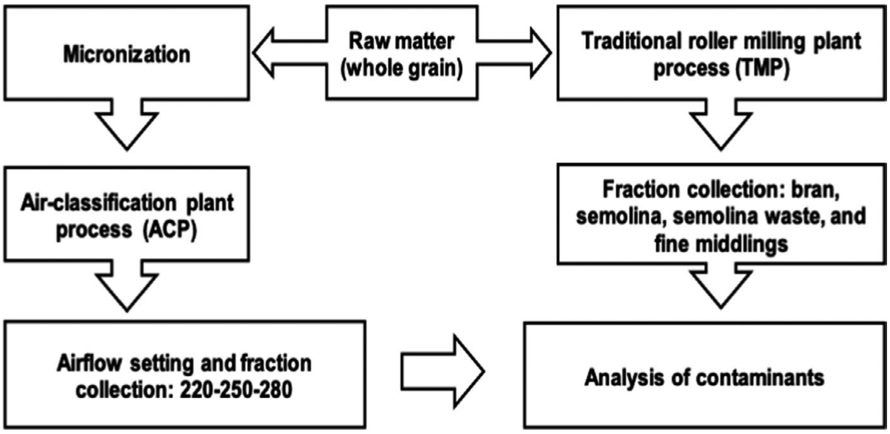

**FIGURE 1** Flow chart of traditional roller milling, micronization, and air-classification processes used to obtain the fractions of interest; 220–250–280: setting points of the airflow incoming

an airflow variation according to the setting of the inlet valve (220, 250, and 280). The pneumatic transport of the whole milled wheat particles has caused a flow of product along circular orbits wherein a series of ascending air currents have been dosed by different airflow opening conditions' settings, which has allowed a progressive increase of the amount of the air and its connection with the entire milled wheat from 220 to 280 in the setting rate of airflow of the valve.

Due to the combined action of different forces, the most lightweight particles have failed to precipitate and consequently have been rated as a "F" (fine), subdivided into F1 (heavier fine particles), and F2 (lighter fine particles) sub-fractions; the remaining heavier particles have been rated as "G" (heavier gross particles). At the end of the air-classification treatment, the G, F1, and F2 fractions have been collected for each sample; also, particular sizes of all fractions have been measured through certified test sieves (Giuliani Tecnologie S.r.l., Turin, Italy), and the ash content has been assessed by following the aforesaid approach. By comparison, four durum wheat grain samples (cv. Svevo)—from 1.1kg to 2.0 kg each—have been processed with the identical procedure, but all of them have only performed at one selected airflow opening condition. Indeed, the setting rate of the incoming airflow within the air-classification system was the same as for the previously chosen fractions, since it was the most appropriate to achieve the aim of this project.

## 2.4 | Analysis of minerals and deoxynivalenol

Each grain milled samples (Retsch pm 100, GmbH, Germany, accessorized with a "comfort" stainless steel grinding jar with 250ml; a 10mm ø stainless steel grinding ball, set at 200 rpm for 5 min), micronized samples (the whole entire milled wheat), and other first-processing products (which belong to traditional and air-classification plants). The analysis of minerals has been carried out to quantify the concentration level of calcium (Ca), phosphorus (P), potassium (K), sodium (Na), magnesium (Mg), iron (Fe), copper (Cu), cadmium (Cd), lead (Pb), and nickel (Ni): All the grain samples have been processed to estimate the concentration of each element in the source material.

Therefore, every sample has been subjected to an initial phase of acid digestion by the use of an economical high-pressure microwave oven in the laboratory (Mars plus CEM, Italy) employed with a 1,800 W energy output; approximately, 200 mg per every dry sample has been directly implanted in a microwave-closed tubes (100 ml PFA HP-500 Plus), two milliliters of 30% (w/w) $H_2O_2$ (Merck, Darmstadt, Germany), 0.5 ml of 37% HCl (Merck), and 7.5 ml of $HNO_3$ (Merck) and 69% of the entire solution have been added to each vessel. Also, a predigestion has been carried out with 7.5 ml of $HNO_3$ at 67% v/v for one hour. Afterward, a 0.5 ml HCl amount has been added and left to act for an additional hour; in conclusion, 2 ml of $H_2O_2$ has also added and left to digest for 30 min, with an entire final volume of 10ml. At the end of the predigestion process, the acid solution obtained has been mineralized within the microwave, the heating program has been performed through a single step: Temperature has regularly increased from 25℃ to 180℃ in 37 min, preserving it at 180℃ for 15 min afterward.

At the end of the digestion procedure and the subsequent cooling process, the three samples have been transferred into a Teflon® beaker, and their entire volume had turned into 25ml with high-purity water (18 MΩ/cm) from a Milli-Q water purification system (Millipore, Bedford, USA); the digest solution have consequently filtered (DISMIC 25HP PTFE syringe filter, pore size = 0.45 mm, Toyo Roshi Kaisha, Ltd.) and stored within a screw cap plastic tube (Nalgene, New York, USA). Furthermore, each experiment has been carried out three times more. The super pure grade reagents, employed for the microwave-assisted digestions, were as follows: hydrochloric acid (36% HCl), nitric acid (69% $HNO_3$), and hydrogen peroxide (30% $H_2O_2$); highly pure water (18 MΩ/cm) has been used for the standards' dilution and to prepare samples throughout the chemical procedure.

Trace elements' quantifications have performed by using an Inductively Coupled Plasma Optical Emission 184 Spectrometer (ICP-OES) with an axially configuration (8,000 DV, Perkin Elmer) equipped with an ultrasonic nebulizer; the Limit of Detection (LOD) for each analyzed element (μg/kg) has resulted: 8.0 (Ca), 2.0 (P), 20.0 (K), 2.0 (Na), 2.0 (Mg), 0.2 (Fe), 0.1 (Cu), 0.3 (Cd), 3.0 (Pb), and 0.9 (Ni).

To assess the trace elements' concentration level, the calibration standards have been prepared and equally treated to samples before dilution (multi-element standard solution, CaPurAn, CPAchem, Stara Zagora, Bulgaria). For detection, it has been necessary to employ the frequency with the lowest interferences regarding every single element: Mg 279.0 nm, Cd 228.8 nm, Fe 259.9 nm, Cu 324.7 nm, Ca 317.9, P 213.6, Pb 220.3, Na 588.9, Ni 231.6 nm, K 766.4, through a specific accuracy analyzed with the use of ERM-BC21 (the European reference material).

Every main milling product derived from the traditional plant, and the fractions obtained from the air-classification system have been further sampled according to representative criteria and then assayed for the DON content (EC Regulation 401/2006). According to the aforesaid criteria, it is assumed that that specific content (consequently divided into the three sub-samples) was the same for the grain sample employed for the roller milling process (TMP); the analysis has been carried out by using the enzyme-linked immuno-sorbent assay (ELISA) (Ridascreen® DON method, R-Biopharm AG, Darmstadt) with a limit of detection (LOD) of 18.5 μg/kg. The recovery range stated in the method was 85%–110%. Deionized water has been acquired from Water Purification System Zener Power I (Human Corporation, Seoul, Korea). The Basic Robotic Immunoassay Operator (BRIO, SEAC, Radim Group, Florence, Italy) has been successfully employed and the absorbance data have been acquired by Sirio-S Microplate Reader (SEAC, Radim Group, Florence, Italy). The ELISA methodological process for the DON assay content in durum wheat samples had already been submitted to a validation phase through the comparison with the chromatographic (HPLC) analysis (Brera et al., 2009).

The RIDA® Soft Win software (R-Biopharm A Darmstadt, Germany) has been employed to quantify the DON in those samples.

### 2.5 | Statistical analysis

The employed samples for the cv. Anco Marzio's experimental project have involved a TMP trial as control ($n = 1$) and both micronization ($n = 3$) and ACP trials: These latter have been carried out with a 220, 250, or 280 setting rate for the airflow. All the collected fractions ($n = 3$) have been analyzed according to the content of the contaminants. The air-classification performance of the F 250 fraction has been further tested by comparing yield and ash contents with samples of cv. Svevo ($n = 5$); the variance analysis has been made applying ANOVA (post hoc: Tukey test) and using the STATISTICA software for the results deriving from elemental analysis and PAST 2.12 for data referring to the DON content (Hammer et al., 2001): In the latter circumstance, the LOD half detection limits (9.25 μg/kg) have been employed for the results below (Anon, 2003).

## 3 | RESULTS AND DISCUSSION

### 3.1 | Technological results (TMP and ACP processes)

The cv. Anco Marzio sample was submitted to the traditional roller milling plant (TMP) for a preliminary evaluation from both milling and technological point of view, through the measurement of yield and ash contents within the main milling fractions. The equivalent sample was further intended as a reference since compared to the results reached from the ACP process. Overall, the results referred to the TMP employment have substantially confirmed the expected performance: More specifically, the entire recovery of the sum of all fractions achieved due to the whole milling products amounted to 96.87% of the initial grain sample with a total loss of matter, which was equal to 3.13%. Furthermore, the yields of the fractions obtained were: semolina (at 37.95%), coarse bran (at 17.65%), refined bran (at 14.45%), fine middlings (at 13.51%), and purified offal (at 13.31%); the results obtained have substantially been those expected by taking into account the variability according to quality and features of the raw matter (Troccoli et al., 2000). In particular, the semolina fraction was compliant with the current national regulations mainly regarding the ash content (<0.90% db), with an average value of 0.83% ± 0.005 (*SD*) on dry basis (Presidential Decree 187/2001). Due to the employment of the micronizing process, high yield values have been measured for all the three trials that have been carried out (average value ± *SD*: 97.48% ± 0.81—Table 1). Moreover, good yields have been achieved for F1 fractions at all the opening airflow setting conditions (220, 250, and 280), which were extremely appropriate for the F1 250 (93.70%) and F1 280 (95.18%) fractions, whereas the F1 220 fraction has been obtained at the 60% value (63.98%) above: Furthermore, the G 220 fractions have shown a maximum value of 33.06%; the entire recovery yield of each opening airflow condition has reached high values between 97.13% and 98.44%. In addition, the F2 fractions have not been further considered to achieve the purpose of this project, essentially due to the scarce amount collected (range: <0.01%–0.68%) in each assessed condition: Therefore, they have been considered inappropriate to carry out the expected analytical assessments. The percentage of the most important particle size according to a technological viewpoint (between 180 μm and 425 μm)—with a range from 10.68% to 14.64% (G) and from 41.73% to 61.46% (F1)—within the assayed opening conditions of the flow. Since the presence of bran particles within the air-classified fractions, the range size between 180 μm and 425 μm included not less than a minimum part of the refined bran fractions (<180 μm, 180 μm, and 250 μm), a rather efficient detail for a better quality of pasta added with bran fractions (Alzuwaid et al., 2020); furthermore, the positive effects of medium coarse and coarse particle sizes of semolina for the end product (pasta) quality had been already analyzed by the experts Sacchetti et al., 2011; also, the attention has been focused on both F1 and G fractions that have been assessed for the ash content, which is a properly appropriate trait of fewer refined products (according to Flagella, 2006 and Padalino et al., 2015). The percentage of the ash content regarding the dry basis has revealed the following average values (±*SD*): 2.04 ± 0.003 (F1 220), 1.84 ± 0.021 (F1 250), 1.80 ± 0.002 (F1 280), 1.28 ± 0.002 (G 220), 1.19 ± 0.011 (G 250), and 1.23 ± 0.009 (G 280). According to these parameters, the statistical analysis has shown a considerable difference ($p < .05$) between F1 250/280 and G 220 fractions: The first mentioned have resulted of great interest due to its slightly high ash content (i.e., fewer refined product) than semolina added to the milling yield showed, whereas G 220 referred to a good performance pointed out in the air-classification procedure; however, the two F1 250 and 280 fractions have

**TABLE 1** Weights (kg), yields (%), and particle size range percentages of the main milling products through the micronizer and air-classification plant (ACP) of durum wheat sub-samples (cv. Anco Marzio)

| **Micronization process** | | | |
|---|---|---|---|
| | **Trials ($n = 3$)** | | |
| **Sub-samples** | **I** | **II** | **III** |
| Starting weight (kg) | 1.0000 | 3.0000 | 1.0000 |
| Micronized weight (kg) | 0.9832 | 2.9226 | 0.9670 |
| Yield (%) | 98.32 | 97.42 | 96.70 |
| Main yield (%) ± *SD* 97.48 ± 0.81 | | | |

| **Air-classification process** | | | | | | |
|---|---|---|---|---|---|---|
| **Airflow opening degree** | **220 (I)** | | **250 (II)** | | **280 (III)** | |
| **Fractions** | **Weight (kg)** | **Yield (%)** | **Weight (kg)** | **Yield (%)** | **Weight (kg)** | **Yield (%)** |
| G | 0.2926 | 33.06 | 0.1000 | 3.42 | 0.0276 | 2.85 |
| F1 | 0.5662 | 63.98 | 2.7384 | 93.70 | 0.9204 | 95.18 |
| F2 | 0.0060 | 0.68 | 0.0002 | 0.01 | 0.0040 | 0.41 |
| Total | 0.8648 | 97.72 | 2.8386 | 97.13 | 0.9520 | 98.44 |

| **Airflow opening degree** | **220 (I)** | **250 (II)** | **280 (III)** |
|---|---|---|---|
| **Fractions** | **Particle size range (425 µm > Ø > 180 µm) (%)** | | |
| G | 11.44 | 14.64 | 10.68 |
| F1 | 61.46 | 41.73 | 45.10 |
| F2[a] | – | – | – |

*Note:* G, heavy gross fraction; F1, intermediate fraction; F2, fine fraction.

[a] Insufficient quantity.

substantially resulted equivalent for analogous parameters regarding ash and milling yield. Nevertheless, that slight difference in the ash content has been considered as a trend toward a higher fiber content, as well as a valuable key feature for a fewer refined product; in addition, the F1 250 fraction has been deemed appropriate for a more specific analysis. Regarding the milling yield and ash content, additional data have been acquired comparing the F1 250 fraction—that referring to cv. Anco Marzio ($n = 1$)—and the F1 250 fractions referring to the air-classified samples belonging to cv. Svevo ($n = 4$); regarding the whole samples ($n = 5$), for F1 250 the average values obtained for the percentage of the yield and ash content were 88.41% ± 3.13 (*SD*) and 1.99 ± 0.14 (*SD*), respectively: Therefore, it has been possible by saving a good performance reached for the two parameters even in the case of different cultivars employed.

## 3.2 | Analysis of minerals (ICP-OES)

Minerals are generally classified as macroelements (i.e., Ca, K, Mg, Na, P) and microelements (i.e., Fe, Cu, Co, Zn, Mn, Mo, Cr, Se) based on the recommended daily intake (respectively around 100 mg/die). If inhaled, by skin contact or ingestion, some trace elements might be potentially noxious to human health (Fernández-Caliani et al., 2019).

The TMP process has reduced Ca values both in semolina (−52%) and in the semolina waste (−39%); in fine middlings fractions, the Ca content has been characterized by a 10% reduction, whereas in bran fractions it has remained unchanged. Beneath the ACP process, a significant difference in Ca content has been detected in F1 and G fractions, obtained by operating at 220, if compared to the other two 250 and 280 conditions, which have been more substantial for F1 220—analogous to more than 36%—and for the G 220 fraction—equal to more than 9%.

The results regarding the TMP employment highlight that P has been maintained in the bran fractions (8.8 mg/kg), whereas its content significantly has decreased in semolina with a reduction up to 95%: analogously, the P trend to an improved content in bran-rich fractions has been highlighted through the ACP employment. Furthermore, the F1 220 and 250 fractions, which are those with the highest content of the aforesaid element, despite the fact that a significant reduction of respectively 63% and 70% if compared to the whole grain. In addition, the P presence in F1 and G fractions set at 280 has not endured a significant difference, probably due to a higher homogeneous distribution within those two fractions.

**TABLE 2** Mean content values ($n = 3$) of the minerals analyzed in the main fractions of durum wheat samples

| | Traditional roller milling plant (TMP), (mg/kg) (db) referred to each type of fraction | | | | | Air-classification plant (ACP), (mg/kg) (db) referred to each type of fraction | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Minerals | Whole grain | Bran fraction | Fine middlings | Semolina | Semolina waste | Micronized sample | F1 220 | G 220 | F1 250 | G 250 | F1 280 | G 280 |
| Ca | 296.6 bc | 309.4 bc | 266.1 c | 141.7 de | 181.2 d | 135.1 bc | 404.7 a | 325.7 ab | 271.3 cd | 150.3 e | 203.3 d | 232.5 d |
| P | 28.7 a | 8.8 bc | 5.1 de | 1.3 f | 3.4 def | 11.1 b | 10.5 b | 6.2 cd | 8.5 bc | 2.2 ef | 4.6 de | 3.7 def |
| K | 1999.0 a | 1,218.6 de | 1951.2 a | 701.9 f | 2038.3 a | 1731.9 ab | 1,377.1 d | 1557.1 bc | 1632.3 b | 1,114.4 e | 2033.0 a | 1508.3 c |
| Na | 716.1 a | 507.2 c | 753.6 a | 67.3 d | 109.1 d | 508.6 bc | 511.0 bc | 479.3 c | 483.3 c | 517.8 bc | 485.1 c | 638.2 a |
| Mg | 618.2 bc | 890.7 a | 437.3 def | 156.5 g | 400.2 ef | 626.4 bc | 725.4 b | 465.1 def | 554.9 cd | 350.8 f | 548.7 cd | 429.6 def |
| Fe | 31.3 b | 39.2 a | 41.1 a | 13.2 d | 18.0 c | 25.5 bc | 23.9 bc | 24.3 bc | 43.0 a | 16.7 c | 26.0 bc | 27.5 bc |
| Cu | 33.5 a | 5.8 bcd | 4.8 bcd | 1.5 f | 2.9 de | 7.3 bc | 7.9 b | 4.3 cd | 6.8 bc | 2.4 e | 3.2 de | 2.9 de |
| Cd | 0.6 a | <L.R. | 0.5 ab | <L.R. | <L.R. | 0.5 b | 0.2 c | <L.R. | 0.1 d | <L.R. | 0.1 d | <L.R. |
| Pb | 3.4 b | 0.7 d | 1.0 cd | <L.R. | <L.R. | 3.0 b | 5.5 a | 0.5 d | 1.4 c | 0.5 d | 0.4 d | 0.1 d |
| Ni | 1.8 bc | 0.4 e | 0.4 e | <L.R. | <L.R. | 1.5 c | 2.4 a | 1.0 d | 2.1 ab | 0.2 f | 0.5 e | 0.2 f |

*Note:* Different letters = values not significantly different ($p < .05$).

Abbreviations: G, heavy gross fraction; F1, intermediate fraction; db, dry basis; LOD, limit of detection.

The bran section derived from the TMP process has highlighted a significant K decrease when compared to the whole grain sample; a higher K reduction has been registered by the fraction related to the semolina (−65%): It might have been possible due to the conditioning phase adding of water. On the contrary, the K content has substantially remained identical with fewer differences in each ACP fraction.

The TMP milling treatment has caused an increase of the Na content within the fine middlings fraction: a 5% higher than the Na amount of the entire wheat, whereas it has been fundamental to notice a highly relevant decrease in semolina (−91%). However, each result regarding the air-classified products has highlighted a decrease in the Na within all the fractions obtained with different airflow opening conditions, except for the G 280 fraction that does not significantly differ from the Na content within the whole analyzed grain.

When the TMP treatment was completed, the amount of Mg increased by +44% in the bran fractions whereas the same element decreased by −75% in semolina, considering the Mg content in the initial entire grain. Regarding the ACP technology, a substantial maintenance of Mg has been detected in the F1 fraction, whereas the same element has significantly decreased in all G fractions, with the minimum amount in G 250 (350.8 mg/kg) equal to 43% of loss in relation to the whole grain.

The TMP employment caused a higher Fe presence both in the bran fractions and in the fine middlings (+25% and +31% each) differently from the Fe value in the whole grain sample, whereas the same element has shown a 58% decrease in semolina fraction. Furthermore, the ACP process' outcome has shown an unchanged Fe content in F1 and G fractions, except for the 250 condition that showed a + 37% increase with the F1 fraction and a −47% decrease in the G fraction. Thus, that trend toward the maintenance or increase of macroelements and iron in every single fraction containing bran particle material (e.g., pericarp and aleurone) has confirmed the interest in rich-in-fiber food (Brouns et al., 2012).

Copper (Cu) has shown a comparable decreasing trend in all parts both regarding the TMP and the ACP procedures: A huge amount of Cu has been lost (−93%) in the G 250 section.

In addition, Cd has not been detected in the analyzed parts, except for the fine middlings: Here, the Cd concentration has not changed. The ACP process has led to a total reduction of the Cd element in the G fractions, and its localization in the F1 parts; a decreasing trend of content has occurred along with the increase of the airflow opening rate (−67% in F1 220 and – 83% in F1 250), with a minimum value in F1 280 equal to 91% of abatement: This factor might be considered as a technological effect on the processed matrix.

As confirmed by the Pb localization in the tegument layers of the kernel, the same element has been detected only in bran (0.7 mg/kg) and fine middlings fractions (1.0 mg/kg): that coincides with the previous outcomes (Bruggemann and Kumpulainen, 1995). Moreover, the ACP procedure has registered a high Pb concentration decrease in each fraction, except for the F1 220 condition—which has identified a + 60% increase—and a significant −59% reduction in F1 250.

Analogously to the Pb trend, Ni content has not been undetected in semolina, whereas a more than 75% decrease has been reached both in the bran fractions and in the fine middlings; in the ACP processing, the Ni concentration was higher both in the F1 220 and F1 250 fractions with an increase of 33% and 16%, respectively.

The outcomes have shown a non-negligible effect within the procedure, starting from the whole grain sample to the micronized sample regarding P, Na, Cd, and Cu: The latter element has resulted highly reduced along the aforesaid passage, and these differences—which might be caused by the employment of pilot plants within the wheat process—indicate that additional studies are required.

Overall, the distribution of contaminants within the milling fractions includes several factors, among which the opening contamination rate is highly important (Cheli et al., 2010). In this study, the outcome has highlighted a different trend regarding the content of minerals in fractions between air-classifier (ACP) and traditional milling (TMP) processes (Table 2). In the first case, the evaluation of the distribution trend in F and G fractions should consider the presence of bran particles within all fractions, although in different amounts and types. Conversely, in the second case (TMP) the marked difference of distribution between the bran-free semolina and the remaining bran-containing fractions was evident: In particular, the majority of the analyzed macroelements (Ca, K, Na, and Mg)—except of P and Fe—have resulted more concentrated in all bran-containing fractions, such as bran, middlings, and semolina waste. This detail might be caused by the high content of minerals in the outer layers structures, above the aleurone that constitutes the phosphorus reserve within the phytates form, and all of them end up in the bran particles (Brouns et al., 2012; Ficco et al., 2020; Madsen & Brinch-Pedersen, 2020). However, a loss of P has occurred in the TMP rich-in-bran parts, and even in the micronized fraction during the ACP process. Nevertheless, although this event might not be completely explained, several factors—such as process effects, sampling, and sample treatment before milling—might have been involved.

A possible explanation to the whole analyzed heavy metals decrease—except for Cd—might be found in a marked effect during that procedure due to the peculiarly constructive features of the experimental system employed: the latter factor—which is at the basis of the not negligible process's effects, and complicated to be completely explained—has already been highlighted in literature, though it requires further investigations (Cubadda et al., 2003).

## 3.3 | Analysis of deoxynivalenol (DON)

As far as the DON mycotoxin presence within the traditional milling products is concerned, further detailed information is available (Brera et al., 2013); therefore, this project has concentrated on the mainly important milling fractions, such as semolina, sum of coarse bran and refined bran compared with the air-classified fractions (Figure 2); in particular, a significant reduced presence (−29.3%) of DON in semolina (558 μg/kg)—compared to the whole micronized sample (789 μg/kg)—has been pointed out, whereas a considerable higher average concentration (1,064 μg/kg) within the entire bran fraction has been detected (+34.9%): that represents a further confirmation of the already acquired information regarding the distribution of DON within the wheat kernel structures and the role the external teguments have since they are a first defensive line against a pathogenic fungi's attack

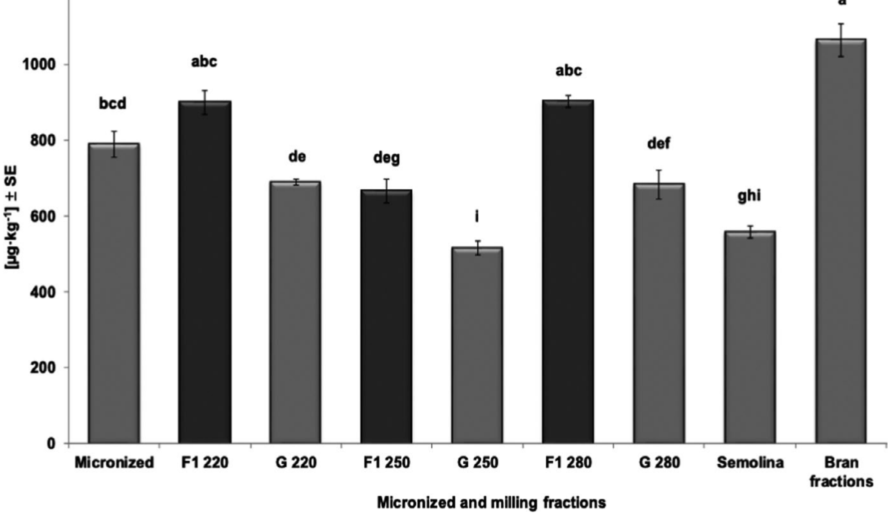

**FIGURE 2** Mean values of repeated analysis ($n = 3$) of DON content ± SE (corrected for recovery) of the main fractions (cv. Anco Marzio) from traditional milling plant (semolina and bran fractions), air-classification plant (F and G fractions at several setting conditions), and micronized samples

(Rios et al., 2009; Visconti & Pascale, 2010). Furthermore, it might clarify the outcomes regarding the micronizing and air-classifying processes. Within the F1 parts obtained by operating in each of the three different airflow opening conditions (220, 250, and 280), the residual bran content was superior than the G fractions, as confirmed by the measurement of the ash content within each type of fraction as already explained. As expected, the range of the average DON concentration (666–899 μg/kg) has had an increasing trend if compared with the G fractions (515–689 μg/kg), which have shown a decrease if compared to the micronized sample (789 μg/kg). Thus, it has been possible to analyze the smaller but substantial differences of mycotoxin accumulation in F1 250 (666 μg/kg), equal to −16% in relation to the micronized sample, and in G 250 (515 μg/kg) in relation to the corresponding opening airflow conditions (220 and 280) left: The F1 250 fraction has proved that it is the most appropriate for the purposes of this project focused to fewer refined end products (e.g., pasta) in relation to the F1 220 and the 280; in addition, the G250 has provided good outcomes for an eventual manufacturing employment due to the lowest accumulation of DON; however, it has shown a reduced content of bran residues, greater content of semolina and fewer transformation yield in relation to the corresponding F1 fraction. After considered this, both the −16% reduction of the average DON content in the F1 250 fraction and the irrelevant +19% increase in relation to semolina necessitate to be intended as outcomes referred to an initial sample with a DON content that does not exceed the mandatory limits (durum wheat: 1,750 μg/kg).

Therefore, the application of the air-classification technology might be a satisfactory method for innovative products during the first durum wheat processing phase to obtain a safer milling fraction than the entire milled wheat in terms of DON content. However, this argument necessitates further analysis.

## 4 | CONCLUSIONS

The minimally processed wheat food improvement in consumption—a healthy parameter for humankind, needs innovative mixtures with high-quality properties; it is a challenge that requires a proper technology for grain fractionation, in such a way to efficiently separate negative and positive features. The outcomes reached with this project have allowed to identify an air-classified fraction (the F1 250), which is the most proper choice for an excellent transformation yield, a good content of bran residues and the maintenance of several macroelements (Ca, K, Mg) and Fe. In addition, a significant decrease of toxic trace elements (i.e., Cd and Pb) has occurred; in the same fraction, a remarkably reduced content of deoxynivalenol has been detected in relation to the micronized sample, which has resulted almost similar to semolina.

In conclusion, these outcomes have provided a valid response to the increasing demands regarding healthier not highly refined food: A better raw matter exploitation might prove to be an added value for both food industry and end users through the employment of milling by-products.

## ACKNOWLEDGEMENTS

The whole group of authors wishes to thank Alessandra Arcangeli and Roberto Mortaro for their precious and fundamental technical support. Open access funding provided by Universita degli Studi di Ferrara within the CRUI-CARE Agreement.

## CONFLICT OF INTEREST

It is necessary to state that there is no conflict of interest regarding this project.

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**How to cite this article:** Cammerata, A., Marabottini, R., Allevato, E., Aureli, G., & Stazi, S. R. Content of minerals and deoxynivalenol in the air-classified fractions of durum wheat. *Cereal Chemistry*. 2021;98: 1101–1111. https://doi.org/10.1002/cche.10458