Journal of Food Composition and Analysis xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

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

Original research article

Transfer of major and trace elements along the “farm-to-fork” chain of different whole grain products

Ambrogina Albergamo[a,b], Giuseppe Daniel Bua[a,b], Archimede Rotondo[a], Giovanni Bartolomeo[a,b], Giovanni Annuario[c], Rosaria Costa[a,*], Giacomo Dugo[a,b,c]

[a] *Dipartimento di Scienze Biomediche, Odontoiatriche, e delle Immagini Morfologiche e Funzionali (Biomorf), University of Messina, Messina, Italy*
[b] *Science4Life s.r.l., a Spin-Off of the University of Messina, Messina, Italy*
[c] *Co.Ri.Bi.A., Consorzio di Ricerca sul Rischio Biologico in Agricoltura, Palermo, Italy*

ARTICLE INFO

Keywords:
Food analysis
Food composition
Cereals
Pseudocereals
Food processing
ICP-MS
Chemometrics

ABSTRACT

An ICP-MS validated method was employed for monitoring major and trace elements along the “farm-to-fork” chains of whole grain (WG) KAMUT®, common buckwheat and durum wheat, considering the different steps of pasta production, and the cooking procedure as well. A PCA analysis identified the elements responsible for sample discrimination, thus providing potential markers of food quality and safety. Stone milling of grains was responsible for maintaining high mineral contents in the downstream products of all the chains, thus defining their WG nature (mean losses in the range of 1.08–5.52% were tracked). Pasta making affected to a greater extent the elemental profile of the different types of pasta, probably due to bronze extruders and long-time drying processes (mean enrichments between 4.00% and 90.08% were monitored). Pasta cooking induced the most severe elemental enrichments (22–225%) and losses (7.70–84.90%) in the “ready-to-eat-product”, as a consequence of complex chemical transformations underlying moisture gain and leaching events. Overall, WG common buckwheat grains, flour and pasta resulted the major source of valuable minerals (*e.g.* Mg, Ca, P, Mn, Fe, Cu and Zn) and the minor source of contaminants (*e.g.* Ni, Cd, and Pb), when compared to the WG durum wheat and KAMUT® counterparts. Nevertheless, the Sicilian durum wheat (cultivar Simeto) chain was marked by a precious content of Se.

1. Introduction

Due to the evolution of different eating patterns and to an increasing consumers’ demand for healthier foods, food industry has progressively moved toward the development of “naturally functional” foods. Among them, cereal products, preferably whole grain (WG), may provide health benefits, including blood glucose regulation and obesity control (Slavin, 2003). Besides conventional cereal crops, ancient minor cereals and pseudocerals are increasingly appreciated and employed for special dietary uses. The minor cereal KAMUT® khorasan, and the pseudocereal common buckwheat have been already investigated for their flavor properties (Costa et al., 2017) and functional components, such as dietary fiber, resistant starch, vitamins, minerals and phenols (Belton and Taylor, 2002). In particular, it has been widely pointed out that both KAMUT® and buckwheat may represent a richer source of healthy major and trace elements than conventional cereals, including durum wheat (Sofi et al., 2013; Piergiovanni et al., 2009a; Ikeda and Yamashita, 1994).

However, similarly to durum wheat, KAMUT® and buckwheat are generally consumed in the form of processed (cooked) goods, which may be characterized by reduced amounts of micronutrients, (*e.g.* minerals), and increased levels of contaminants, (*e.g.* heavy metals), compromising their quality and safety (Slavin et al., 2000). Progression of grains through the processing chain up to the consumer could be reasonably investigated considering pasta as the final product of the “farm-to-fork” chain, since it is typically produced by means of a standardized process, mainly consisting of grain milling and pasta making steps (Cubadda et al., 2009). It is generally assumed that roller mills typically exploited by the milling industry reduce consistently the content of micronutrients originally present in grains, while pasta making and cooking may be responsible for minor losses or gains of minerals and heavy metals, due to potential release events from the equipment, as well as contamination processes (Cubadda et al., 2009; Cubadda et al., 2005; Cubadda et al., 2003). During conventional milling, the outer layers of grains- typically rich in inorganic micronutrients- are discarded, whereas the starch-rich white endosperm is

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[*] Corresponding author at: Dipartimento Biomorf c/o Scienze Veterinarie, University of Messina, Viale Annunziata, 98168 Messina, Italy.
E-mail address: costar@unime.it (R. Costa).

https://doi.org/10.1016/j.jfca.2017.12.026
Received 22 April 2017; Received in revised form 11 December 2017; Accepted 13 December 2017

Please cite this article as: Albergamo, A., Journal of Food Composition and Analysis (2017), https://doi.org/10.1016/j.jfca.2017.12.026

ground to produce a nutritionally depleted “white” flour and, thus, products thereof. However, such drawback may be prevented by “stone grounding” all grain components for obtaining WG flour and derived products, in which bran and germ, along with nutrients and contaminants, should be maintained in the same proportions present in grains (Borneo and León, 2012). Interestingly, a renewed interest in this milling technique has led to a marketing advantage, as evidenced by the recent preponderance of stone milled products both in retail and commercial markets (Posner and Hibbs, 2005).

Although the elemental profiles of “white” flour (semolina) and pasta obtained along the industrial chain of durum wheat were successfully elucidated (Cubadda et al., 2009; Cubadda and Raggi, 2005; Cubadda et al., 2003), no works have yet focused on the transfer of micronutrients and contaminants during the artisanal production of non-conventional WG pasta. Major and trace elements in food are suitably determined by inductively coupled plasma (ICP) techniques (Licata et al., 2012; Lo Turco et al., 2013). However, beside multi-element detection capability shared by ICP-based approaches, inductively coupled plasma mass spectrometry (ICP-MS) is characterized by much lower detection limits and wider linear dynamic ranges, allowing it to be considered as the technique of choice for the elemental profiling of food matrices (Albergamo et al., 2016; Bua et al., 2016a,b; Di Bella et al., 2015; Naccari et al., 2015; Salvo et al., 2016). Also, chemometrics is feasibly implemented to complex ICP-MS data with the intent to extract latent information by large datasets avoiding redundancy, and to identify one or more variables which could be used for sample discrimination (Vadalà et al., 2016; Salvo et al., 2014).

Within this context, the present work aims to tracking the evolution of the elemental profile in the “farm-to-fork” chain of WG KAMUT® and common buckwheat, considering the respective grains, flours and pasta. A conventional WG durum wheat chain was also investigated for comparative purposes. A set of 18 major and trace elements was determined in the selected matrices during milling, pasta making, and cooking processes, to assess which elements are more susceptible to the considered steps, as well as which step plays a central role in affecting their levels.

The tracking of inorganic micronutrients and contaminants along the processing chain by ICP-MS associated to multivariate methods, may be a potential tool useful to industries and inspection agencies for ensuring the quality and safety control of such functional foods.

2. Material and methods

2.1. Chemicals and standard solutions

Argon (99.9990% purity) and helium (99.9995% purity) were supplied by Rivoira S.p.A. (Milan, Italy). HNO_3 (65% v/v) and H_2O_2 (30% v/v) were of Suprapur grade (Mallinckrodt Baker, Milan, Italy). Ultrapure water ($< 5\,mg\,L^{-1}$ TOC) was obtained from a Barnstead Smart2Pure 12 water purification system (Thermo Scientific, Milan, Italy). Stock solutions of the internal standards Ge, In, Sc, and Bi, as well as of investigated major (Na, Mg, K, Ca and P) and trace elements (Fe, Cu, Mn, Zn, Se, Ni, Mo, Cr, Co, V, As, Cd and Pb) ($1000\,mg\,L^{-1}$ in 2% HNO_3) were purchased from Fluka (Milan, Italy). A Reference Material (durum wheat flour, RM8436) from the National Institute of Standards and Technology (NIST, Gaithersburg, USA) was employed for accuracy tests. Before use, polyethylene equipment for sample collection, handling and storage, as well as laboratory glassware and polytetrafluoroethylene digestion vessels were decontaminated by washing with 5% HNO_3 for at least 12 h, rinsing with ultrapure water, and then drying.

2.2. Analytical instrumentation

A closed-vessel microwave digestion system (Ethos 1, Milestone, Bergamo, Italy) was employed for the sample acid digestion. Determinations of major and trace elements were carried out by iCAP Q (Thermo Scientific, Waltham, MA, USA), a quadrupole ICP-MS, equipped with an ASX-520 autosampler (Cetac Technologies Inc., Omaha, NE, USA). Quartz plasma torch and nickel sampler and skimmer cones of 1.1 and 0.5 mm were used. Thermo Scientific Qtegra™ Intelligent Scientific Data System software was employed for instrumental control and data acquisition.

2.3. Experimental plan

2.3.1. Samples

Organic WG KAMUT® (*Triticum turgidum* L. ssp. turanicum), grains (KAM-G), flour (KAM-F) and short pasta (KAM-P), as well as organic WG common buckwheat (*Fagopyrum esculentum* Moench, cultivar La Harpe) grains (Buck-G), flour (Buck-F) and short pasta (BuckP), were withdrawn at different stages along the relative processing chains, belonging to an Italian company producing minor cereal and pseudocereal based products. Similarly, organic WG durum wheat (*Triticum turgidum* L. ssp. durum, cultivar Simeto) grains (DW-G), flour (DW-F) and short pasta (DW-P) samples were obtained from a Sicilian company specialized in high-quality pasta production and supply. In all three cases, a unique batch of grains was followed along the relative processing chain (Fig. 1).

2.3.2. Milling process

Each grain batch was dry-cleaned to remove stones, broken grains and other foreign matter unsuitable for milling (Fig. 1). Then, cleaned grains were milled by means of granite (KAMUT® and common buckwheat batches) and flint (durum wheat batch) stone mills. No water-tempering was required before milling. Obtained by a theoretical extraction rate of 100%, the three flours were subsequently employed in the pasta making processes (Fig. 1). However, aliquots of each WG flour were sampled in decontaminated polyethylene vessels and they were stored in the dark, at room temperature, no more than 7 days.

2.3.3. Pasta making and cooking

Each type of flour (1 kg) was mixed with tap water at room temperature, to produce doughs with a moisture of 33% for WG KAMUT® and common buckwheat, and 31.5% for WG durum wheat. An aliquot of the water employed by each pasta production plant was withdrawn at this step. Hydrated doughs were subjected to a slow bronze die extrusion, with a constant temperature of 45 °C for WG KAMUT® and common buckwheat, and 50 °C for WG durum wheat. Subsequently, slow drying process was performed by means of low temperature drying cycles (36 h at 35 °C for WG KAMUT® and common buckwheat; 24 h at 40 °C for WG durum wheat) to obtain three types of artisanal short pasta, which were sampled in decontaminated polyethylene vessels (Fig. 1). Once in laboratory, 100 g aliquots of each pasta (KAM-cookP, Buck-cookP and DW-cookP) were separately cooked in Pyrex beakers by using ultrapure water, according to the cooking times reported on the respective commercial packages.

2.4. Sample preparation and ICP-MS analyses

Aliquots of 500 mg (fresh weight, fw) of each sample, were collected with the help of a nylon/fiberglass spoon (NSF/ANSI STANDARD 51), ground with a teflon mortar to avoid metal contamination (flour samples excluded) and then digested with 8 mL of HNO_3 and 2 mL of H_2O_2. A temperature program of 0–200 °C in 10 min (step 1), and 200 °C held for 20 min (step 2), with a constant microwave power of 1000W was adopted. After cooling down to room temperature, digested samples were diluted up to 50 mL with ultrapure water. Water samples were pretreated with ultrapure HNO_3 (1% v/v). Dry weight (dw) determinations were performed for each sample on separate 100-g aliquots by oven drying at 103 °C until constant weight.

Before ICP-MS analyses, the instrument was tuned to obtain the