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DETERMINATION OF MACRO ELEMENTS IN GLUTEN-FREE FOOD FOR CELIAC PEOPLE BY ICP-OES

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Abstract
This paper is the first analytical approach to the study of seven nutrients in the gluten-free foods for celiac people. The ICP-OES technique was used. One of the advantages about the use of ICP-OES for this characterization is the high selectivity and low interferences for studied elements.
The concentration values of K, Li, Sr, Na, Ca, Mg and Al in seventeen gluten-free food samples are reported. Considering the average concentrations of the elements analyzed, excluding lithium, in the present study it can be concluded that they are inadequate if compared with the recommended daily intake by international organisms, providing only from 1.5 to 20% of the RDI for the essential metals. In particular, we can suppose that, many celiac people consume small quantities of potassium which contribute to regulate blood pressure and prevent hypertension.
The tolerable upper level intake is exceeded by consuming more than 200 grams of gluten free bread during a day.

Keywords: gluten-free foods, nutrients, metals, ICP-OES, celiac

1. Introduction

The significance of consumption of macro elements on human dietary, and their effects on human health is well documented (World Health Organization, 1996) [1]. Several information are available on the chemical composition of food for no celiac people, but unfortunately, few data are reported on the composition of gluten free food. As recently reported in literature, the number of celiac disease is growing as well as the prevalence in elderly people is becoming evident [2]. The only available action is a lifelong strict gluten-free diet, which leads to restoration of the atrophied intestinal villi.

Several gluten free cereals and pseducereals employed in food preparation for celiac patients are available naturally: rice (*Oryza sativa*), maize (*Zea mays*), sorghum (*Sorghum bicolour*), oat (*Avena sativa*), buckwheat (*Fagopyrum esculentum Moench*) whose flours are the most commonly used. For example, buckwheat [3] is highly nutritious ingredient known as a source of protein with favorable amino acid composition and vitamins starch and dietary fiber, essential minerals [4] and trace elements [3]. However, buckwheat seed has lower concentrations of some metals (Zn, Fe) than the other cereals and pseudocereals. Also, the machining processes on the seeds (dehulling, 4milling, etc.) can significantly change the nutrient composition.

The concentrations of inorganic substances take by dietary are important, in fact, minerals are present in all body tissues and fluids and their presence is necessary for the maintenance of some physicochemical processes which are essential to life [5-7]. Mineral nutrients can be classified into major, secondary and micro or trace minerals [8] on their requirement by humans. Moreover mineral deficiencies or excesses in humans may result in major health problems.

In this context, monitoring usual total nutrient intake is necessary to evaluate adequately the population's nutritional status and adherence to recommendations for nutrient intake [9]. Most gluten-free foods are contain high levels in fat and calories to enhance flavor, texture and appearance [2]. Several authors [10-12] established that many gluten-free products, compared with the enriched wheat products contain lower amounts of thiamin, riboflavin, niacin, folate and iron products that they are intended to replace. The results of a research suggested inadequate intakes of fiber, iron, and calcium in 50% of celiac females studied [10-12]. Today, no data exist on the other essential elements.

The majority of mineral components that must be determined in food samples are present at low concentrations and in the presence of interfering substances; hence analytical techniques [13,14] with adequate sensitivity and selectivity are required for their accurate determinations. Additionally, it is important to remember that the accuracy of the quantitative analytic procedure is strongly dependent on the sampling and sample preparation steps [8,15]. The instrumental techniques are the most employed for element analysis in foods (AA, ICP-OES, ICP-MS, etc.) are those based on atomic spectrometry and inorganic mass spectrometry.

In the present work, we report and discuss the experimental results obtained through Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) measurements performed on a set of twenty-seven gluten free food samples. The aim of this research was to characterize the mineral composition (Na, K, Ca, Mg, Al, Li, Sr) in 27 different commercial gluten free food produced and usually sold in Italy (pasta, breads, flours, etc.). Moreover, to investigate the daily intake from diets according to references intake levels (DRI) [5], in this study we have compared to nutritional properties of gluten free food with the recommended daily intake by international organisms.

2. Experimental

2.1 Quality control and quality assurance

All the vessels and flasks were cleaned before use by rinsing three times with HNO_3 (1%) and three times with Milli-Q water. All the analyses of metals in gluten-free food samples were repeated three times and the relative standard deviation results ranged from 2 to 5%. Every week, blanks were analyzed to demonstrate that the treatment used for cleaning vessels and flasks is suitable to obtain the quality assurance required in this study.

The repeatability, calculated as the relative standard deviation (RSD%) of three independent measurements of a multi-elemental standard solution at 10 $\mu g \cdot L^{-1}$, ranged from 0.2 to 5.0%. The repeatability of the whole method, calculated as the relative standard deviation (RSD%), for three independent analysis of independent portions of the same sample, ranged from 0.5 to 10%. A blank was run up every five samples. All data reported were blank corrected.

2.2 Samples

Twenty-seven samples of gluten-free products (pasta, biscuits, flours, etc), produced in Italy were collected in 2013 from markets and pharmacies in Palermo city (Italy). Only the bread and breadsticks were produced in local (Palermo and neighborhood) bakeries. The samples selected were representative of the Italian market. Samples were milled and homogenized by using a food processor (plastic-coated) and then sub-sampled for analysis. Samples were handled immediately or stored in the refrigerator at 4°C until analysis for a period of less than 24 h. From each gluten-free food sample, three aliquots were digested by microwave system and each sample solution was analyzed in triplicates.

2.3. Sample digestion

Gluten free food samples were dried at 50ºC in an oven with air-circulation until it reached constant weight. Later, about 0.2 g dried and ground sample was digested by using 2 mL of 65% HNO3 (Fluka, Milano) and 1 mL of 35% H_2O_2 (Fluka, Milano) in a closed microwave system (Milestone model MLS-1200 Mega, Milestone Laboratory Systems, Italy). The instrumental conditions used for the microwave digestion were: 1 min at 250 W, 1 min at 0 W, 5 min at 250 W, 5 min at 450 W, 3 min at 600 W and 5 min at 300 W. The volumes of the mineralized samples were completed to 25 mL with Milli-Q water (R>20 MΩ cm^{-1}) (Merck Millipore) and mineral concentrations were determined by inductively coupled plasma-optical emission spectroscopy.

2.4 ICP-OES analysis

The ICP-OES analysis of macro nutrients was performed in radial viewing mode. Instrumental conditions are listed in Table 1.

Table 1 - ICP-OES operating conditions	
RF power (W)	1300
Sample uptake flow rate (mL min-1)	1.5
Gas flow rates (L/ min-1)	Auxiliary: 0.2; Nebulizer: 0.8;Argon: 15
Viewing mode	Radial

Table 2 - Wavelengths used for elemental determinations by ICP-OES		
Element	Wavelength 1 (nm)	Wavelength 2 (nm)
Al	396.153	308.215
Ca	317.933	315.887
Li	670.783	610.365
Mg	285.213	279.077
K	766.490	404.721
Na	589.592	330.237
Sr	407.771	421.552

The quantitative analysis was performed at two different spectral lines for each element (Table 2). The concentrations of the metals reported in this paper have been calculated considering the average of the concentrations obtained at the two wavelengths that, for all analytes, differed by less than 6%. The detection limit (LOD) and the quantification limit (LOQ) were estimated as reported in previous papers [13-16] and respectively ranged from 3 to 10 µg L^{-1} and from 10 to 33 µg L^{-1} by IUPAC criterion. Calibration standard solutions were prepared by dilution with HNO_3 2% of a multi-element calibration standard solution (Perkin Elmer Pure Plus, Atomic Analytical Standard containing 29 elements. The concentration range of the calibration curves was between 10 and 2000 µg L^{-1}. For calibration, a solution of HNO_3 2% as blank was used. The analysis of the six standard solutions was replicated in every ten samples. Correlation coefficients of the calibration curves were in the range from 0.9995 to 0.9999. To eliminate memory effects related to the previous sample analysis, between two subsequent samples, a 25 s washing was settled. A blank was run up every eight samples. All reported data were blank corrected.

Sodium, potassium, calcium, magnesium, aluminum and lithium were determined in each sample, chosen on the basis of their significance in the study of gluten-free food.

3 Results

Table 3 shows the concentration values of K, Li, Sr, Na, Ca, Mg and Al in the different gluten-free food samples representing a variety of popular brands targeted for celiac people. Results are reported as mg kg^{-1} of dry sample. In figure 1 are shown the percentages of minerals in analyzed gluten free food samples.

Potassium was detected in all analyzed food and the concentration ranged from 14 to 3747 mg kg^{-1}. The highest contents were found by us in the samples n°14 (flour for cakes) (3747 mg kg^{-1}), n°25 (croutons) (2479 mg kg^{-1}) and in the two local bread samples (n°19 and n°20) (1327 and 1082mg kg^{-1}). The mean K concentration was 716 mg kg^{-1} and is very lower those measured in Hispanic products that showed K concentration in the interval 4000 and 5000 mg kg^{-1} [17-19].

The **lithium** content in analyzed samples ranges from 2.6 to 248 mg kg^{-1}. The mean value was 20 mg kg^{-1} and the highest Li concentration was found in a croutons sample (n°25). Levels of lithium in food consumed by the Canarian people were found as follows: milk 1.4 mg L^{-1}, grain 4.4 mg kg^{-1} ; potatoes 1.3 mg kg^{-1}; fish 3.1 mg kg^{-1}; fruit 1.4 mg kg^{-1}; vegetables 2.3 mg kg^{-1} [19].

The **strontium** concentration in analyzed gluten free food ranged from 0.2 to 102 mg kg^{-1}. The highest strontium content (102 mg kg^{-1}) was found in egg noodles (sample n°7) and the lowest (0.2 mg kg^{-1}) in the Pasta fusilli (sample n°5).

Table 3 - Metal concentrations (mg Kg^{-1} d.w.) in gluten free food samples							
Sample	K	Li	Sr	Na	Ca	Mg	Al
1 Pasta	250	3.0	6.6	1205	5	102	21
2 Noodles	331	19	2.5	409	133	423	0.8
3 Flour	208	2.8	6.2	905	57	86	16
4 Biscuits	635	2.8	6.1	1986	69	280	18
5 Pasta fusilli	386	8.0	0.2	306	106	359	0.6
6 Pasta Linguine	611	2.9	6.3	923	5	207	19
7 Egg noodles	211	15	102	793	272	373	1.5
8 Finger biscuits	109	43	4.5	1136	340	291	1.7
9 Buckwheat biscuits	1238	2.7	6.0	4172	105	495	17
10 Croutons	14	4.5	78	808	265	256	1.3
11 Rice noodles	131	2.8	6.3	682	237	224	9.5
12 Couscous	940	2.6	5.8	838	100	247	18
13 Corn couscous	905	2.7	48	874	196	273	16
14 Flour for cakes	3747	2.8	6.2	5427	1658	813	10
15 Lasagna	1171	2.8	6.2	4071	1098	210	14
16 Corn flakes	855	2.7	6.0	5245	123	160	1.0
17 Dietetic biscuits	73	9.1	12	909	826	231	1.0
18 Breadsticks	322	68	3.5	3209	374	1207	1.5
19 Local bread B.	1327	5.8	19	10383	1682	317	12
20 Local bread P.	1082	2.8	6.2	12315	490	308	13
21 Corn flakes	855	2.7	6.0	5245	123	160	17
22 Shortbread	72	25	3.5	792	264	279	1.0
23 Biscuits	33	7.7	2.0	382	1288	436	1.4
24 Butter cookies	42	15	56	1134	40	314	1.2
25 Croutons	2479	248	36	5816	637	441	13
26 Egg biscuits	195	40	3.9	1070	297	30	12
27 Industrial bread	1115	2.9	13	10520	361	456	23
Mean value	716	20	17	3021	413	333	10

The sodium content of the gluten free food samples ranged from 306 to 12315 mg kg^{-1} with average of 3015 mg kg^{-1} and, the highest sodium levels were measured in three bread samples. The sodium concentrations in the analyzed samples are very high, for example the mean Na concentration in some Hispanic wheat cultivars varied significantly between 41.0 and 273 mg kg^{-1} [20].

The concentration of **calcium** in gluten free food samples ranged from 5 to 1682 mg kg^{-1}. The mean value was 413 mg kg^{-1}. The highest values were detected in the samples n° 19 (Local bread B) (1682 mg kg^{-1}), n°14 (Flour for cake) (1658 mg kg^{-1}) and n°23 (Biscuit) (1288 mg kg^{-1}), while the lowest concentrations were found in two pasta samples (n°1 and n° 6).

The range of **magnesium** values found in gluten free food samples was 30-1207 mg kg^{-1}. The mean value was 333 mg kg^{-1}. The highest values were detected in the samples n° 18 (breadsticks) (1207 mg kg^{-1}) and n°14 (flour for cakes) (813 mg kg^{-1}).

The **aluminum** content of the gluten free food samples ranged from 0.6 to 23 mg kg^{-1} with average of 10 mg kg^{-1} and is in agreement to those (0.4-13 mg kg^{-1}) determined by Greger [21,22] in cereals. In our case, the highest Al levels were measured in two pasta samples (n°1, n°6). Considering that Al additives are contained in specific processed foods, contrary to our expectations, the lower concentrations (about 1 mg kg^{-1}) were found in some foods (n°8, n°10

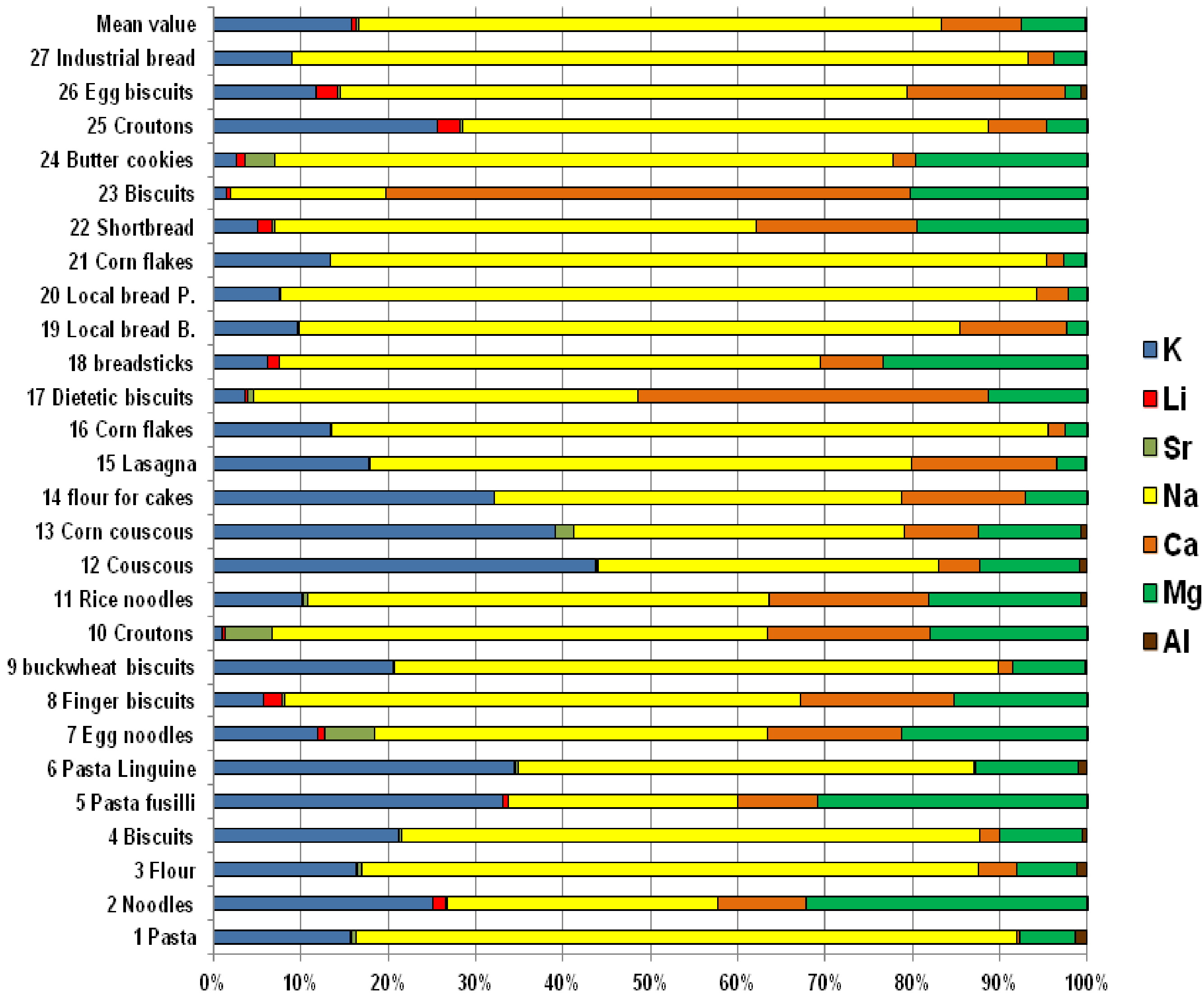

Figure 1 - Percentages of single nutrients in the analyzed gluten free food

n°, n°17, n°22, n°23, n°24) that generally, in foods with gluten, contain additives. $NaAl_3H_{14}(PO_4)_8$ is used in the food industry as a leavening agent in baked goods and $Na_8Al_2OH_2(PO_4)_4$ as an emulsifying agent [23]. The concentrations of Al in convenience and fast foods analyzed by some researches [24] ranged from 0.85 to 38 mg kg^{-1}, refereed to fresh weight of the edible portion are higher than gluten free food.

Aluminum in food has several origins: may be a natural contaminant in vegetal and animal organisms; may be a contaminant during industrial food processing; use of Al-containing additives; may come from kitchenware used for food preparation and/or serving stocking and packaging food materials.

3.1 Chemiometric considerations

Considering that treatment of the raw data is an important step in extracting and obtaining useful information, before chemometric analysis, data were pretreated by mean centering. The data set of seven analytes concentration was subjected to PCA, using concentrations as dependent variables, two factors with initial eigenvalues greater than one were found. Factors one and two yielded 55.2% of explainable results, yielded with Na, K, Ca, Mg and Li loading heavily on the first factor, and Sr and Al loading heavily in factor two. Scores plot for this data is presented in Figure 2, illustrating separations from different food categories (bread, biscuits and snacks).

By using scatter plot (Figure 3) for aluminium and sodium data it is possible to note that for some food samples, the aluminium values are greater than other values. Interesting to highlight that, by comparing to industrial bread (sample n°27) with local breads, (sample n°19 and n°20 respectively) high aluminium value was founded. These different values can be ascribed at different yeast used in bread production, for instance natural yeast in local bread and industrial yeast,

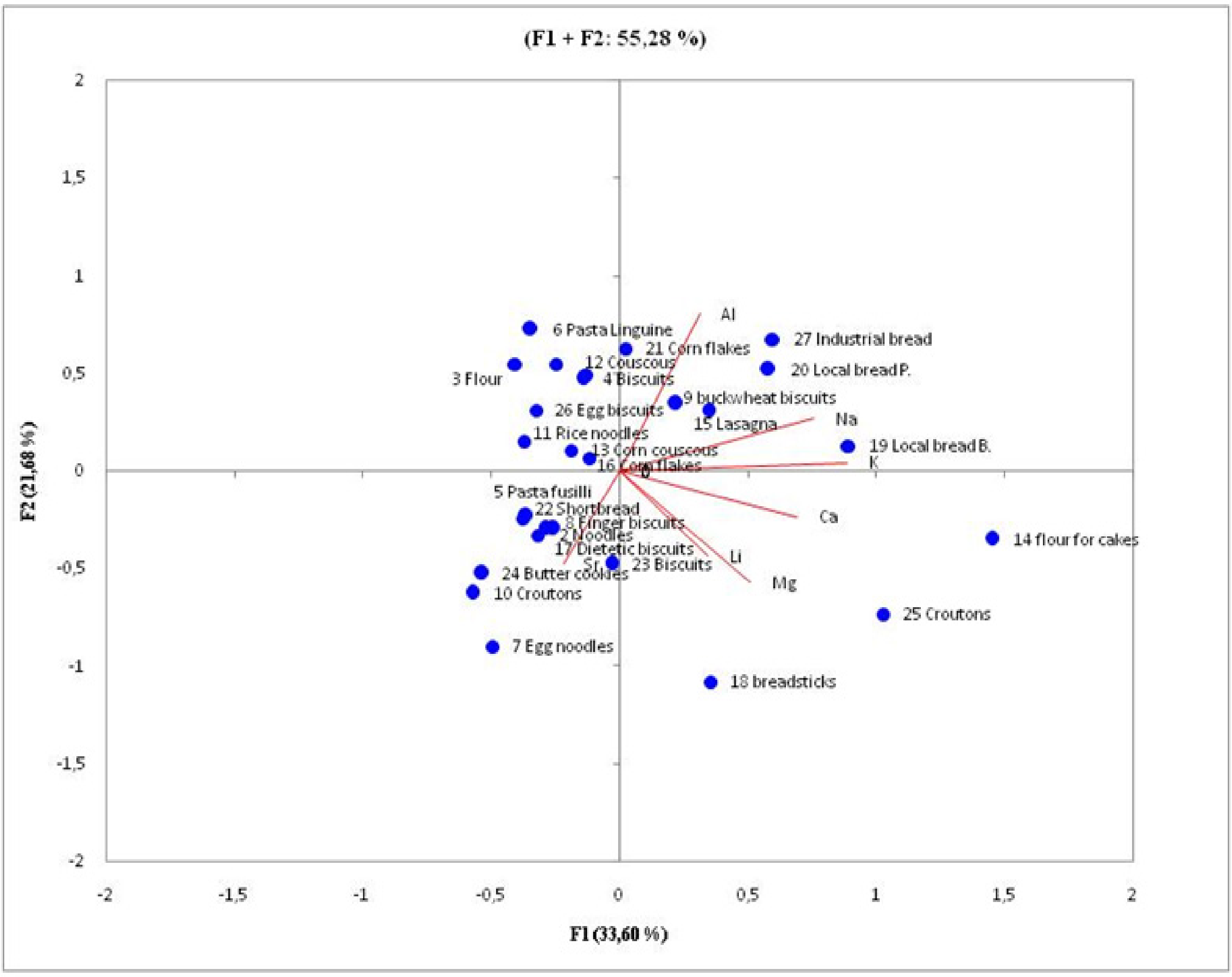

Figure 2 - Score plot of analytical data

containing aluminium as $NaAl_3H_{14}(PO_4)_8$ form, in industrial bread.

3.2 Enrichment factor

The enrichment factor (EF) [24,25] can be used to discriminate the metals originating from human activities and those from natural sources and to assess the degree of anthropogenic influence. Element enrichment factor, evaluated relative to the background values, was used to establish which elements were relatively enriched in the different gluten-free food samples. Values of EF close to 1 pointing to a natural origin while those greater than 10 are considered to have a non-crustal source [24]. Five contamination categories are recognized on the basis of the enrichment factor (Table 4).

In our case, the enrichment factors ranged from $1 \cdot 10^{-5}$ to 13.8. In detail, the sample n° 25 (croutons) showed the highest value of EF (14) for the lithium, followed (3.8, 2.4) by samples n° 18 (breadsticks) and n°8 (finder biscuits).

Table 4 - Contamination categories based on EF values

EF > 2	Deficiency to minimal enrichment
EF 2-5	Moderate enrichment
EF 5-20	Significant enrichment
EF 20-40	Very high enrichment
EF > 40	Extremely high enrichment

For sample n°25 the value reflects a significant enrichment while for the other a moderate enrichment.

3.3 Dietary intake (DI)

Considering the effects of dietary on human health, is very important and great interest to obtain data about daily intake of macro elements for celiac population. The daily intake (DI) depends both on the amount of elements in the food and the quantity consumed.

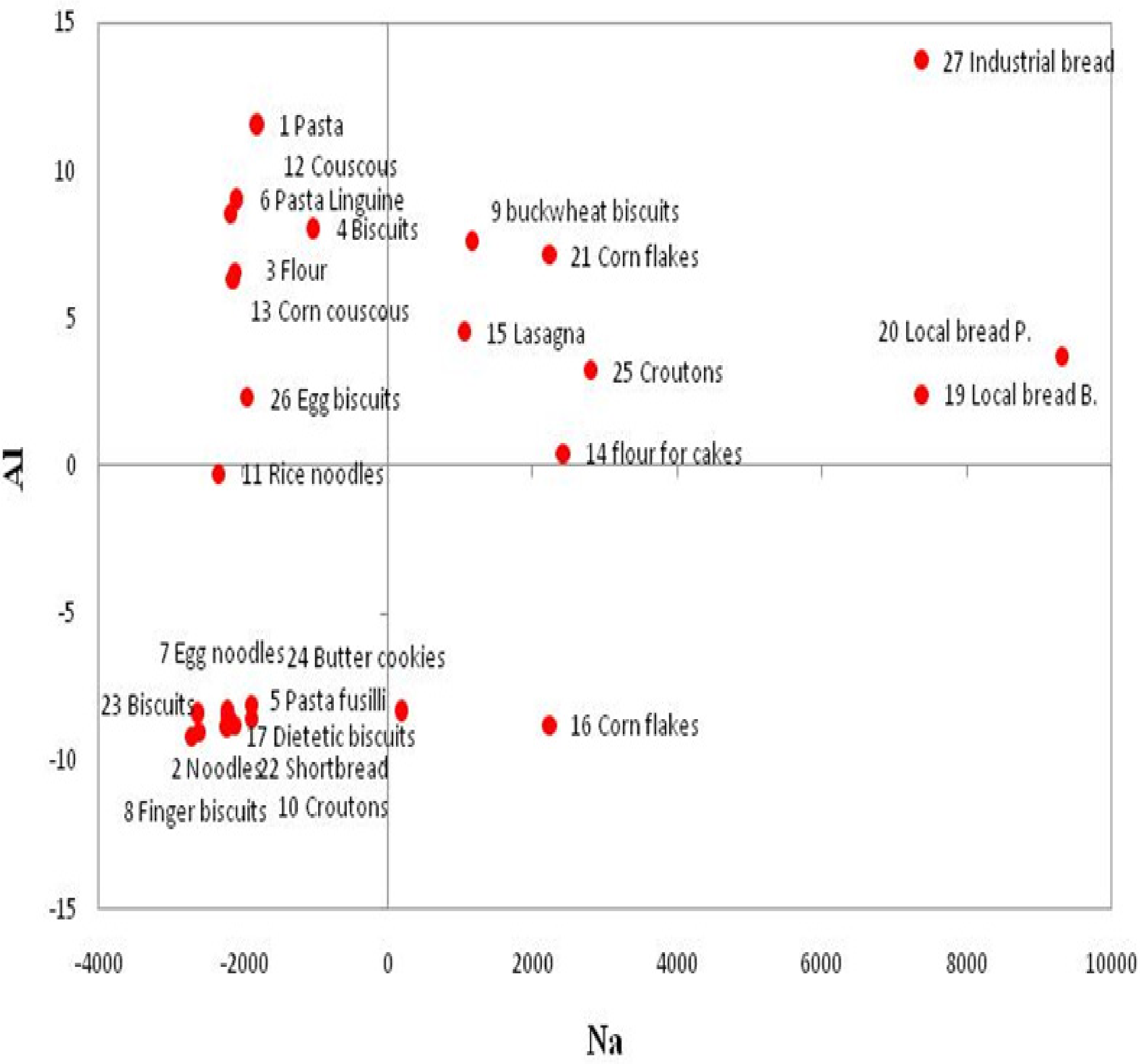

Figure 3 - Scatter plot for aluminium and sodium

The main food of Italian celiac consumers is bread, pasta and food prepared using flours, hence metal levels in cereals and additives contribute a major part to the total daily intake. DI intake of metals was calculated as reported in equation 1.

$$DI = (C_{metal} \times D_{food\ intake}) \quad (1)$$

where C_{metal} and $D_{food\ intake}$ represent the heavy metal concentrations in gluten-free food and daily intake of food respectively. Dietary intake levels for celiac people were estimated for essential nutrients (Table 5) consuming daily amount of 100 g day^{-1} of gluten-free food. These supplies (Figure 4) from 0.03 to 8.0 % of potassium, 14–1234% of lithium, 2.5-82 % of sodium, 0.1–17% of calcium, 0.7-29 % of magnesium for male and 0.9-38% for female of the Reference Adequate Intake (RDA) for people adults (31-50 years) (Figure 4) [5].

The AI for K is set at 4700 mg day^{-1} in adults [26]. This amount through dietary intake maintains lower blood pressure levels, reduce the adverse effects of sodium chloride intake on blood pressure, reduce the risk of recurrent kidney stones and possibly decrease bone loss. People must habitually and regularly consume potassium because the body does not preserve it and K must be available during prolonged periods of dietary deprivation or abnormally increased external losses through excretion by the kidneys or gastrointestinal tract [7,26]. The Dietary Reference Intake (RDI) for **potassium** is similar for males and females, thus, considering the mean values concentrations of all the samples analyzed, celiac people may obtain about 1.5% of their RDI from gluten free foods. For K, the lowest RDI (0.03%) values were obtained for the samples n°10 (croutons), (0.07%) n° 23 (biscuits) and (0.09%) n°24 (butter cookies). Hard potassium deficiency is characterized by

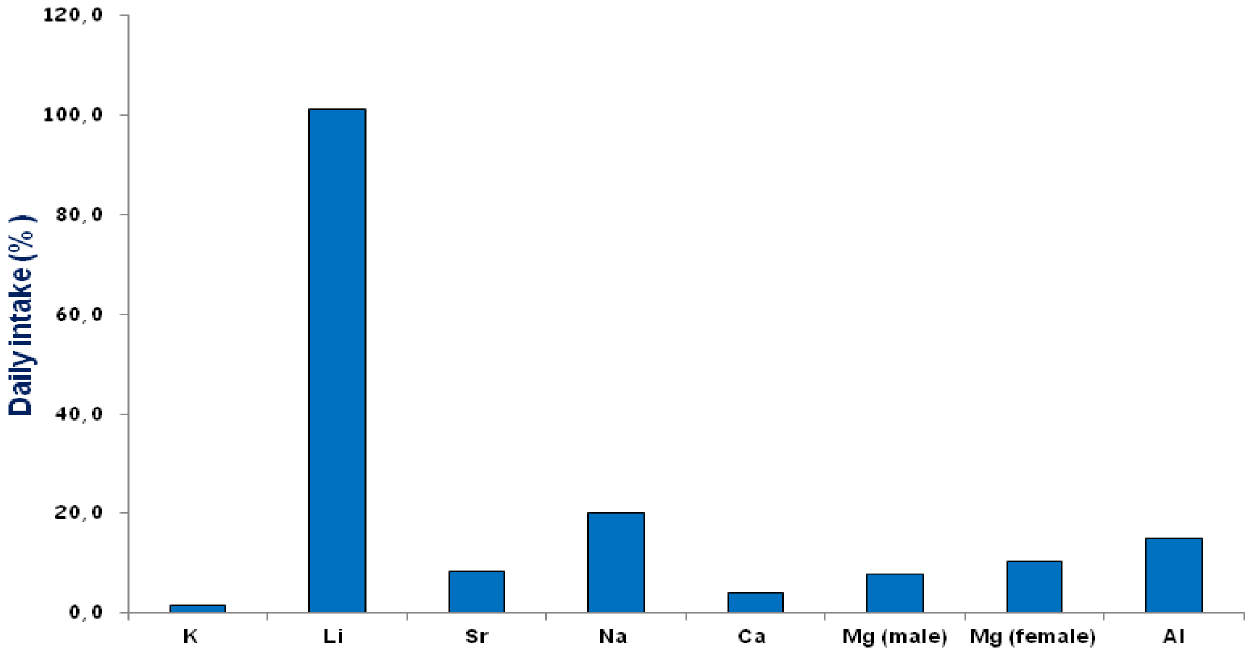

Figure 4 - Mean percentage of Adequate Intake for nutrients (consuming 100 g of gluten free food)

hypokalemia, a serum potassium concentration of less than about 140 mg L^{-1}. The adverse consequences of hypokalemia include cardiac arrhythmias, muscle weakness, and glucose intolerance. Moderate potassium deficiency, which typically occurs without hypokalemia, is characterized by increased blood pressure, enlarged salt sensitivity, enlarged risk of kidney stones and increased bone turnover, monitored by greater urinary calcium excretion. A scarce intake of potassium by diet may also increase the risk of cardiovascular disease, particularly stroke. Inadequate potassium intake can result from a deficiency of its conjugate anions (for example citrate that in the body is transformed to bicarbonate). Consequently an insufficient intake of K is also linked with reduced intake of bicarbonate precursors.

Calcium is the fifth most abundant element in the Earth's crust as part of several minerals and an essential nutrient. Calcium should accordingly be in a chemical structure easily available for dietary intake. Osteoporosis, the disease in which bones become fragile and more likely to fracture due to low bone density caused by loss of calcium minerals, affects millions people worldwide. This hidden epidemic has a predominant incidence in north-western Europe and is becoming increasingly significant with the ageing of the population.

The recommended daily allowance of calcium is around 1000 mg day^{-1} for adults, with recommendation varying between countries [27-28]. Greater needs are required during growth, and needs progressively decrease with age [29]. Enhanced calcium needs prevail during pregnancy and lactation [30]. The tolerable upper Ca intake amount ranges from 1000 to 3000 mg day^{-1}, based on Ca excretion or kidney stone formation.

Considering the mean values levels of the analyzed samples, celiac people may obtain about 4.1 % of their RDI from gluten free foods. For calcium, the lowest RDI values were obtained for two pasta samples (n°1 and n°6). The richest food sources of calcium, among those analyzed, were local bread (n°19) and a flour for cakes (sample n°14) accounts for only the 17% of the daily requirement of this very important nutrient.

Magnesium has several roles in the human organism, and some of its more important health benefits comprise regulating the contraction of muscles, the production of proteins, and even the production and transportation of energy throughout the body [7,31]. It reduces the risk of developing cardiovascular disease. In a recent study, Stipanuk and Caudill [31] found that people who consume water deficient in Mg were far more likely to develop cardiovascular disease [31]. Magnesium, also has a role in the occurrence of arteriosclerosis, diabetes, obesity, metabolic syndrome and hypertension [7,32]. Diets high in magnesium (fruits and vegetables) may create an alkaline environment, reducing Ca excretion and

Table 5 - Percentage of contribution to Daily Reference Intake for nutrients in gluten-free food samples.								
Sample	K	Li	Sr	Na	Ca	Mg (male)	Mg (female)	Al
1 Pasta	0.5	15	3	8.0	0.1	2.4	3.2	31
2 Noodles	0.7	97	1	2.7	1.3	10	13	1.1
3 Flour	0.4	14	3	6.0	0.6	2.1	2.7	23
4 Biscuits	1.4	14	3	13	0.7	6.7	8.8	25
5 Pasta fusilli	0.8	40	0	2.0	1.1	8.6	11	0.9
6 Pasta Linguine	1.3	14	3	6.2	0.05	4.9	6.5	27
7 Egg noodles	0.4	73	51	5.3	2.7	8.9	12	2.1
8 Finger biscuits	0.2	214	2	7.6	3.4	6.9	9.1	2.4
9 Buckwheat biscuits	2.6	14	3	28	1.1	12	16	25
10 Croutons	0.03	23	39	5.4	2.7	6.1	8.0	1.9
11 Rice noodles	0.3	14	3	4.5	2.4	5.3	7.0	14
12 Couscous	2.0	13	3	5.6	1.0	5.9	7.7	26
13 Corn couscous	1.9	14	24	5.8	2.0	6.5	8.5	23
14 Flour for cakes	8.0	14	3	36	17	19	25	15
15 Lasagna	2.5	14	3	27	11	5.0	6.6	20
16 Corn flakes	1.8	14	3	35	1.2	3.8	5.0	-
17 Dietetic biscuits	0.2	45	6	6.1	8.3	5.5	7.2	-
18 Breadsticks	0.7	341	2	21	3.7	29	38	2.1
19 Local bread B.	2.8	29	10	69	17	7.6	9.9	17
20 Local bread P.	2.3	14	3	82	4.9	7.3	9.6	19
21 Corn flakes	1.8	14	3	35	1.2	3.8	5.0	24
22 Shortbread	0.2	124	2	5.3	2.6	6.6	8.7	1.4
23 Biscuits	0.07	39	1	2.5	13	10	14	2.0
24 Butter cookies	0.09	76	28	7.6	0.4	7.5	9.8	1.7
25 Croutons	5.3	1239	18	39	6.4	10	14	19
26 Egg biscuits	0.4	201	2	7.1	3.0	0.7	0.9	17
27 Industrial bread	2.4	14	6	70	3.6	11	14	34
Mean value	1.5	101	8.4	20	4.1	7.9	10	15

thus improving bone density [33]. The Dietary Reference Intake (RDI) for males and females is considered to be 420 mg day^{-1} for male and 320 mg day^{-1} for female. Considering the mean value concentrations of all the samples analyzed, while males may obtain as much as 29% of their RDI from gluten free foods the contribution to RDI for females is 38%. For Mg, the lowest RDI value (0.7%) was obtained for the egg biscuit sample (n° 26). Magnesium deficiency is the cause of most depression and related mental health problems.

Sodium is the main positive ion of the extracellular fluid and functions as the osmotic determinant in regulating extracellular fluid volume and thus plasma volume. About 95% of the total sodium of the body is found in extracellular fluid. Sodium is also an important determinant of the membrane potential of cells and the active transport of molecules across cell membranes. Sodium and potassium are essential mineral nutrients [34]. The Adequate Intake for sodium is set for adults at 1500 mg day^{-1} [35] to ensure that the overall diet provides an adequate intake of other minerals and microelements and to cover sodium sweat losses in people exposed to high temperatures or bodily active. This AI does not apply to individuals who lose large volumes of sodium in sweat, such as sports and workers exposed to hard activities.

The AI for sodium for older adults and the elderly is somewhat less, based on lower energy intakes, and is set at 1300 mg day^{-1} for people 50 through 70 years of age, and at 1200 mg day^{-1} for older. The Tolerable Upper Level of Intake (UL) for Na was set at 2300 mg day^{-1} based on blood pressure elevation as documented in dose-response trials.
Considering the mean value concentrations of all the samples analyzed, celiac people may obtain as much as 20% of their RDI from gluten free foods. For sodium, the lowest RDI value (2%) was obtained for a pasta sample (n° 5). In the present study, the tolerable upper level intake is exceeded by consuming more than 200 grams of gluten free bread (samples n°19, n°20 and n° 27) during a day. A small amount of **sodium** is found naturally in foods [36]. In the prepared foods, in variable quantities, sodium is added in the form of sea or rock salt.
The most important undesirable effect of increased sodium intake is elevated blood pressure, which has been known to be an etiologically related risk factor for cardiovascular and renal diseases.
This can easily happen because bread is an essential food in human nutrition. It is a good source of energy, contains vitamins, proteins, lipids and minerals, which are essential in human diet. In Ital, and in Mediterranean diet, bread is a major component of people's.
Aluminum is the most abundant metallic element and constitutes about 8% of the Earth's crust.
It is not recognized if Al is one of the elements essential for the human body because studies on its physiology and toxicity are difficult by its ubiquity and because of contamination risks associated with it [22]. Intake from foods, particularly those containing the element compounds used as food additives, represents the major source of Al for the general people. According to several authors [22], the Al dietary intake must not exceed 6 mg kg^{-1} b.w to avoid potentially toxic levels [22,37]. In 2008, a revised Provisional Tolerable Weekly Intake (PTWI) for all Al compounds in foods, including additives, of 1 mg kg^{-1} b.w. was established by the European Food Safety Authority (EFSA) [38]. It was established in 2008 and confirmed in 2011 that metal could affect the reproductive and developing nervous system at lower doses than those used to establish the previous PTWI of 7 mg kg^{-1} b.w. [39,40]. Mean dietary exposure from water and food in non-celiac people showed large variations between the different countries and, within a country, between different surveys. It ranged from 1.6 to 13 mg Al day^{-1}, corresponding to 0.2 to 1.5 mg kg^{-1} b.w. per week in a 60 kg adult (EFSA). Pennington and Schoen [41] estimated dietary Al intake in USA as 0.7–11.5 mg day^{-1} in children, 8–9 mg day^{-1} in men and 7 mg day^{-1} in women.
The usual Al intake at the mean level of the Belgian adult population estimated to 0.035 mg kg^{-1} b.w. day^{-1} [40]. This value is within the range that has been reported to EFSA among the European countries (0.029–0.214 mg kg^{-1} b.w. day^{-1}) [38] and is particularly close to the exposure level in France with 0.040 mg kg^{-1} b.w. day-1 [42].
Considering the data obtained in the present study, the range of Al daily intake was 0.9- 34%. The highest values (about 30%) were found consuming 100 g of Industrial Bread (sample n°27), Pasta (samples n° 6 and n°20).
Presence of **lithium** has been detected in all kind of food, but those with highest levels are grain and vegetables. For this reason, a dietary intake of this kind of food provides more lithium than a diet rich based on food of animal origin. Lithium does not have a known biological use and does not appear to be an essential element for human life. It is a toxic element for several organs, especially after a long use, and can result in adverse metabolic effects like hypothyroidism, hyperparathyroidism, changes in calcium levels, interferences in the glucose metabolism and weight gain, among others.
Major dietary sources of lithium are grains and vegetables (0.5–3.4 mg Kg^{-1}), dairy products (0.50 mg Kg^{-1}), and meat (0.012 mg Kg^{-1}).There is no specific RDA for lithium, nor is it known how much, if any, we need. Dietary studies estimate that we acquire about 2 mg day^{-1}. The U.S. Environmental Protection Agency (EPA) in 1985 estimated the daily Li intake of an adult (70 kg) to range from 0.650 to 3.1 mg [43]. Considering these data, in present paper we assume 2.0 mg as RDA. Total lithium intake from gluten free food in the Italian celiac population ranged from 0.26 to 26 mg day^{-1} corresponding from 13 to 1239% of RDA. In our case, this limit is exceeded by consuming about 8 grams of gluten free croutons (samples n° 25) during a day.
Total lithium intake in the Canary Islands population was estimated at 3.7 mg day^{-1} [19]. Considering the data obtained in this report, mean lithium intake (2.0 mg day^{-1}) exceeds that in Belgium (0.0086 mg day^{-1}), United Kingdom

(0.016 mg day^{-1}), France (0.0145 and 0.0285 mg day^{-1} for children and adults, respectively) and the one (0.03626 mg day^{-1}) in Vietnam [18]. In Chile where lithium-rich salinas contain up to 1500 mg L^{-1}, the total lithium intake reaches 10 mg Kg^{-1} without evidence of adverse effects to the local population. People on special diets or populations residing in naturally low-lithium areas would require lithium supplements or other appropriate measures to meet adequate intake. Deficiency of lithium is not really known. The theory that a deficiency of lithium can cause an increase in depression has not been adequately proved. Lithium toxicity is a very real problem when it is used as a drug. In the treatment of manic disorders, there is a fine line between therapeutic and toxic levels. Lithium excess produces some symptoms by upsetting the fluid balance and mineral transport across cell membranes. Symptoms of lithium toxicity include nausea, vomiting, diarrhea, thirst, increased urination, tremors, drowsiness, confusion, delirium and muscle weakness. Skin eruptions may also occur. With further toxicity, staggering, seizures, kidney damage, coma, and even death may occur

The mean estimated intake of **strontium** for celiac population was set at 1.7 mg/day. This amount is in good agreement to the intake of this metal for the population of a Spanish Population (Canary Island) settled in the range 1.5-2.0 mg/day [44]. Limited information is available on the toxicity of stable strontium, and there is no direct evidence that no radioactive strontium is toxic to humans under normal environmental exposures. The toxicity of strontium is related to its ability to interfere in biological processes involving calcium, primarily skeletogenesis. Data in the literature [44] indicate that a very high dietary intake of strontium may disturb bone mineralization, which is expressed by a lower bone mineral density and decreased size of bone apatite and calcium content.

3.4 Health Risk Index (HRI)

The Health Risk Index is obtained by dividing daily intake of nutrients by their safe limits [8, 45]. An index more than 1 is considered as not safe for human health. Considering our data, health risk index was lower than 1 for all the samples except lithium in five samples: n°8 (finger biscuits), n°18 (breadsticks), n°22 (shortbread), n°25 (croutons) and n° 26 (eggs biscuits).

4.0 Conclusion

In this paper we present analytical approach to the study of nutrients in the gluten-free foods for celiac people. A total of 27 different foods produced in Italy were investigated. By ICP-OES technique. Gluten-free foods analyzed contain levels of essential elements under the limits tolerated by the law and the contribution of the foods evaluated to the daily intake of all the elements analyzed remain under the recommended levels by international organisms. Considering the average concentrations of some nutrients, excluding lithium, found in the present study it can be concluded that they are inadequate if compared with the recommended daily intake by international organisms, providing only from 1.5 to 20% of the RDI for the essential metals. In particular, we can suppose that many celiac people consume small quantities of potassium which contribute to regulate blood pressure and prevent hypertension.

Therefore, the index of the nutritional quality for gluten-free food products with respect to all the metals seems to be relatively poor. These conclusions are in good agreement to some authors affirming that commercial gluten-free cereal foods, made of refined flours or starches, are of lower nutritional value compared to their wheat counterparts [46].

The information collected in this report and the health risk index also suggest that lithium contamination in five of the analyzed gluten-free food had potential for human health.

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