



Multi-elemental analysis of commercial wheat flours by ICP-MS triple quadrupole in function of the milling degree

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ABSTRACT

This preliminary study is focused on an elemental analysis of 60 samples of different commercial grains' flour, including various typologies of refined product, researching transition metals and trace elements. All the samples were first digested with a microwave digestion system and then analyzed by a triple quadrupole (TQ) inductively coupled plasma mass spectrometer (ICP-MS-QQQ) located in a Clean Room ISO class 6. The minimum value of most of the elements (Li, Be, Na, Ca, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Se, Rb, Sr) are in the wheat flour "00" type and in the wheat flour "0" type (B, Na, Mg, Al, Cu, Ag, Cd, In, Cs, Pb, Bi). On the opposite, the maximum value of these elements is found in whole wheat flour (B, Mg, K, Ca, Mn, Zn, Ga, Rb, Sr, Ba) and in the wheat flour "0" type (Na, Al, V, Cr, Fe, Co, Ni, As). Relating rare-earth elements (REE), all of them show value similar to each other and not under the detection limits thanks to the use of a TQ in the clean room. The final aim is to create a large database, with a high data bank and easily enlargeable, that could be used in future to analyze unknown flour samples and to set up traceability analysis. The purpose of this work is to find some trends of analyzed elements in function of different parameters, such as milling degree or geographical origin, also with a statistical point of view.

1. Introduction

The Regulation (EC) no. 178/2002 of the European Parliament identifies the general principles and requirements of food law, establishes the European Food Safety Authority (EFSA) and all the procedures in the field of food safety (European Parliament, 2002).

To protect food quality, analytical chemistry plays a fundamental role confirming the authenticity of a product, the possible presence of contaminants and any lack of correspondence between the data obtained and those declared (European Parliament, 2002).

In the agri-food area, the identification of "marker" elements to trace the origin of raw materials is a fundamental analytical process widely applied in more and more scientific studies. In the food area, the most significant elements are heavy metals (As, Cd, Hg, Pb, etc.) and transition metals (Cr, Co, Ni, Cu, Zn, etc.), trace elements, lanthanides / rare-earth elements (REE: Ce, La, Eu, etc.) (Telloli, Tagliavini, Passarini, Salvi, & Rizzo, 2023).

Although in very low concentrations, heavy metals are catalysts for

reactions requiring high activation energy which would be impractical without them. In fact, they are not elements that should be considered harmful to humans. We therefore distinguish the heavy metals nontoxic (Iron, Zinc, Copper, Manganese and Selenium), and toxic for human health (Arsenic, Cadmium, Nickel, Lead and Mercury). A peculiar characteristic of heavy metals is their ability to persist in the matrices in which they are found. For this reason, their dispersion causes a large accumulation in the environment and especially in plant products (Zwolak, Sarzyńska, Szpyrka, & Stawarczyk, 2019).

Pb, Cd and Hg are the most abundant toxic trace elements (TTEs) and are potentially present in plants in an ionic/inorganic form. In particular, it has been observed that they have a higher bioaccumulation factor (an index that evaluates the tendency to accumulate in an organism) than in durum wheat compared to other cereals (Ma et al., 2022).

Even at low concentrations, TTEs are dangerous for human health: for example, Pb, Cd, and Hg have a high affinity for the sulfhydryl groups of proteins, resulting in the ability to interfere with the function

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of hundreds of enzymes (Fu & Xi, 2020).

Cadmium is classified as carcinogenic to humans by the International Agency for Research on Cancer (IARC) and carcinogenic and suspected mutagenic by the European Chemicals Agency (ECHA) as it acts as an interfering agent with respect to biochemical functions, mimetic of essential elements such as zinc and calcium and inhibits DNA repair. It can lead to chronic renal failure and prostate, kidney, and lung cancer (Genchi, Sinicropi, Lauria, Carocci, & Catalano, 2020).

Lead is also considered a probable human carcinogen and toxic for reproduction. It competes and interferes with Ca(II) and Zn(II) ions. In this way, thanks also to its organotropism for the brain, bones, and adipose tissue, it is responsible for lead-related disorders, particularly serious in children and young people (McCaffrey & Lynch, 2020).

These contaminants are closely monitored. The European Regulation n. 1881 (European Parliament, 2006) established the maximum levels (MLs) for Pb and Cd at 0.200 mg kg⁻¹ in wheat. MLs are reduced to 0.050 for Pb and 0.040 mg kg⁻¹ for Cd in cereal-based foods for infants and children (European Parliament, 2006).

Heavy metals have increasingly become a focus of public interest thanks to the analytical techniques that have made possible their ultra trace detection (Fu & Xi, 2020).

To carry out a detailed and significant analysis it is therefore necessary to have validated methods and adequate tools to be able to quantify even elements present in small quantities, in traces and ultra-traces such as parts per billion (ppb) or even parts per trillion (ppt).

The analytical techniques most used in food safety are divided into mass spectrometry, spectroscopic techniques, separation techniques. In accordance with scientific literature, among the techniques used in elemental analysis studies, mass spectrometry (ICP-MS or ICP-AES) is the one widely used. In particular, ICP-MS is a very relevant instrument as it provides to quantify over 70 elements at low concentrations (typically in the order of ppb or ppt) in different types of samples (Nardi et al., 2009). The present preliminary study focused on performing a quantitative analysis of trace elements and transition metals within different commercial flour matrices using a triple quadrupole mass spectrometer (ICP-MS-QQQ), as it allows a detailed multi-elemental analysis with a high sensitivity.

Cereals, with about 500 genera and >5000 species, belong to the *Gramineae* family and have been the basis of human nutrition for thousands of years (Poole, Donovan, & Erenstein, 2021).

The success of cereals derives from some characteristics such as caloric value, protein and lipid content, mineral salts, and vitamins, which make them suitable for human consumption; therefore, for these reasons, they are cultivated in all parts of the world: wheat in the Middle East, rice in Southeast Asia, corn in South America, sorghum in Africa. Cereals are the most important food for most of the planet's population, providing about half of dietary protein (Raheem, Dayoub, Birech, & Nakiyemba, 2021).

The most important cereals in the human diet are wheat (*Triticum*), rice (*Oryza sativa*), oats (*Avena sativa*), barley (*Ordeum vulgare*), rye (*Secale cereale*), maize (*Zea mays*) and millet (*Panicum miliaceum*). Of these, wheat is the most consumed and widespread. Together with rice, it represents the basic food for 4/5 of the world's population.

Among the different varieties of wheat, the most important are durum wheat (*Triticum durum*) and soft wheat (*Triticum aestivum*), from which flours mainly derive (Chandra, Bharagava, Yadav, & Mohan, 2009).

Generally, flour is the product of grinding dried vegetable substances. The most important natural flours are obtained from cereals, but also from legumes (beans, broad beans, peas, soy). They have different characteristics depending on the type of grinding and whether they are obtained from the caryopsis with all the layers (e.g., integral) or not. By excluding all the cortical parts (bran and middling) from the milling, white flours are obtained because they are mainly made up of starch. Other components are cellulose, fats, protein substances (especially gluten), water, salts (especially phosphates) and vitamins.

For the same cereal, the differences in composition, and consequently in nutritional value, depend on the greater or lesser separation of the integumentary parts during the milling, i.e., on the degree of sifting, which is the percentage of flour that is extracted from the cereal, eliminating bran and middling.

From a technological point of view, the quality of the flour is based on obtaining a final product with excellent organoleptic properties such as taste, colour, and smell as well as an appropriate level of humidity, correct ash content, particle size and absence of contaminating elements.

According to Italian law n. 580 (Italian Legislation, 1967) the product obtained from the grinding and subsequent sifting of the wheat is divided in different degrees: 50%, 72%, 80%, 85%, which correspond respectively to types "00", "0", "1", "2".

Whole wheat flour is obtained by grinding the whole grain, without subsequent refinement and removal of part of the milled content. According to the DPR n. 187 (Degree of the Italian Republic President, 2001), a flour can be considered integral if it has a residual ash content between 1.3% and 1.7%.

The aim of this work is to research the presence and concentration of trace elements, transition metals and REEs within different matrices of commercial wheat flours. The relative abundance of these elements allows to characterize the flours from a compositional point of view and allows to search for any identifying markers.

Considering the high number of people who use this food for their personal dietary, it is important to highlight the concentration of each elements present. Also, this study wants to investigate if any toxic elements could be found in the wheat flour. The study included 60 different wheat flour products from several manufacturers.

The concentrations of major, trace elements and REEs were determined by Inductively Coupled Plasma Mass Spectrometry with triple quadrupole (ICP-MS-QQQ) located in an ISO class 6 clean room.

2. Material and methods

A total of 60 samples of different kinds of market wheat flour were analyzed. Table 1 reports the different types of samples collected.

2.1. Sample preparation methodology

All the volumetric flasks and beakers used for the preparation of the samples were made of Teflon to prevent losing trace quantities of metal into borosilicate glass.

All the plastic micropipette tips, and the centrifuge tubes were cleaned with nitric acid before use.

All the reagents used in the experiment were analytical-reagent grade.

For each sample, 0.40 g were mixed in a solution with HNO₃ and H₂O₂. TraceSELECT® grade 69% HNO₃ and ultra-pure grade 30% H₂O₂ were acquired from Sigma-Aldrich (St. Louis, MO, USA) and Carlo Erba Reagents (Milan, Italy), respectively.

High purity de-ionized water (resistivity 18.2 MΩ cm⁻¹) was obtained from a Milli-Q Advantage A10 water purification system (Millipore, Bedford, MA, USA).

Different solutions have been tested to verify the best conditions for

Table 1
Number of samples analyzed for each type of flour selected.

Type of flour	Sample number
Wheat 00 type	21
Wheat 0 type	20
Wheat 1 type	7
Wheat 2 type (semi-whole wheat)	3
Whole wheat	9
TOTAL	60

obtaining a complete digestion (Table 2). All the samples were digested with a microwave digestion system, Speedwave Four model (Berghof, Germany), equipped with temperature and pressure control in TFM™-PTFE vessels, following the procedure:

- Constant pressure at 30 bar
- STEP 1: 5-min time
 - o Temperature linear increase from room T to 180 °C
- STEP 2: 10-min time
 - o Maintenance of the conditions reached at the end of the first step
- STEP 3: 5-min time
 - o Power linear increase from 400 to 1200 W
- STEP 4: 5-min time
 - o Maintenance of the conditions reached at the end of the third step.

By subjecting the three test solutions obtained to this digestion program, the following results were obtained:

- Test 1: perfectly mineralized.
- Test 2: not mineralized.
- Test 3: perfectly mineralized.

From these results it can be seen that hydrogen peroxide is essential for the success of the digestion of the flour sample in solution. Between the first and third tests, the first is chosen because it requires smaller quantities of nitric acid and hydrogen peroxide, providing the required result. All flour samples are therefore digested in the solution thus composed and with the previously described digestion program.

After the digestion, the acid mixture was left to cool to room temperature (about 20 min). After checking the clearly of the resulting solution, from the metal grade centrifuge tubes the acid mixture was quantitatively transferred into plastic vials (Falcon® 50 mL Polypropylene Conical Tubes), previously cleaned with nitric solution, and made up to a final volume of 10 mL with H₂O.

2.2. Analytical techniques

All the measurements were carried out in a dedicated Clean Room ISO Class 6, (ISO 14644-1 Clean room), with controlled pressure, temperature, and humidity. This clean room satisfies all the standard requisites for food trace analysis, with a maximum concentration limit of 1×10^6 (particles/m³) for particles $\geq 0.1 \mu\text{m}$ for ISO Class 6 (Telloli et al., 2023).

A Triple quadrupole (TQ) inductively coupled plasma mass spectrometer (ICP-MS-QQQ, 8800 model, Agilent Technologies, Santa Clara, CA, USA), equipped with two quadrupoles, one (Q1) before and one (Q2) after the Octopole Reaction System (ORS3), was installed in the clean room facility.

The instrument operated in the He-mode, using Helium as gas in the reaction and collision cell.

The operating conditions of ICP-MS-QQQ and acquisition parameters are explained in Table S1 (Supplementary Materials).

The multi-element standard solution IV-ICPMS-71 A (10 $\mu\text{g}/\text{mL}$) and the REE standard solution CCS-1 (100 $\mu\text{g}/\text{mL}$) supplied by Inorganic Ventures (Christiansburg, VA, USA) were used for calibration and spike recovery studies.

A series of 10 blanks was prepared, transferring the carrier solution into ten vials used for the analysis.

Table 2

Test solutions for the mineralization of the flour samples.

Test	Flour (g)	HNO ₃ 69% (mL)	H ₂ O ₂ 30% (mL)	H ₂ O (mL)
1	0.40	2.8	3.4	13.8
2	0.40	2.8	–	17.2
3	0.40	10.0	4.0	6.0

2.3. Validation method parameters

Limit of detection (LOD) and limit of quantification (LOQ) for each element were established both for instrument and process, according to EURACHEM recommendation. The first one was obtained from the analysis of five blanks of the instrument with three replicates each. Instrument blank means instrument carrying solution: 2% of HNO₃ and 1% of HCl. The standard deviation was obtained for each element multiplying for 3 (3σ) and for 10 (10σ) respectively for LOD and LOQ. The same consideration was done for LOD and LOQ of the process, analyzing five blanks of the process, with three replicate each. The blank of the process refers to the same quantity, 7 mL plus 1 mL of 69% solution of HNO₃ and 30–32% solution of H₂O₂ respectively, analyzed with ICP-MS-QQQ after a cycle of acid digestion and for each sample mineralized.

2.3.1. Linearity of the external calibration

Two curves of calibration were obtained. One with seven concentrations point in the ppb range: 0, 100, 1000, 5000, 10,000, 20,000, 50,000 ppb, for major and trace elements. The other for REE in ppt range: 0, 0.01, 0.1, 1 and 5 ppt.

2.3.2. Instrument efficiency

Standard Reference Material (SRM) was used as an external calibration standard to verify the accuracy of the technique and the instrument efficiency. For flour samples it was not possible having at certified materials with the same or similar matrices, therefore we chose a different material with a prevailing organic matrix: SRM-1573 A (Tomato leaves) from NIST. The SRM sample was digested and prepared as explained for the samples.

2.4. Multivariate analysis

Statistical analyzes were performed using the software XLSTAT by Addinsoft.

Principal Component Analysis (PCA) is one of the most widely used chemometric techniques that aims to minimize the dimensionality of data. It is applied in various sectors, including chemistry, biology, medicine, economic analysis and even food. PCA has often been applied to food traceability and characterization, including the detection of environment-related contamination.

Multivariate analysis is required to evaluate the huge number of data resulting from ICP-MS-QQQ analysis, allowing to investigate the differences between the samples.

3. Results and discussion

3.1. Method validation

Limits of detection (LOD), limits of quantification (LOQ) and linearity of the external calibration for multi-element trace analysis are reported in Table S2 (Supplementary Material).

Also, the validation of the method using the SRM-1573 A (Tomato leaves) from NIST is reported in Table S3 (Supplementary Material). The experimental concentration obtained in ppm for all elements does not exceed the 15%, compared to the certified NIST value.

The data (LOD, LOQ, linearity and NIST value) confirm the validation of the method and of the instrument, underlining the repeatability of the data in comparison with previous works (Andreozi et al., 2023; Telloli et al., 2023).

3.2. Flour samples data analysis

The elemental profiles of wheat were analyzed using chemometric analysis to investigate if it is possible to discriminate samples from different type of flour.

All elements' concentrations were converted to ppb for homogeneity.

The PCA model was obtained using the first two principal components (PCs), which explained 57.95% of the variance (see Table S4 and the Scree plot in Fig. S1 in the Supplementary Materials).

The biplot obtained from PCA scores is illustrated in Fig. 1, showing that samples are separated into different clusters, confirming the different type of flours.

Type "0" and type "00" flours, however, are not clearly distinguishable. This occurs because the minimum milling difference is probably not sufficient to generate flours with very different values of the elements analyzed. Between these two types of flour the main difference is in the grain size and not in the element content. However, there could be more evident differences considering the REEs, of which wheat flours "00" appear to be richer.

Whole wheat flours (colored in green, at the top of the graph in Fig. 1) are characterized by major elements such as K, Na, Mg, Ca, and Mn but also Sr, Rb and Ba.

Similar trend is shown by the wheat flour "2" type (colored in orange, immediately below the whole wheat samples), which appear to be enriched in Al, Na and B.

In the central part of the graph in Fig. 1 on the left, wheat flour "1" type (colored in gray) appears to be enriched in Li, Se and Bi.

3.3. Element value description

Table 3 shows the minimum, maximum and average concentrations of all the elements analyzed: major and trace elements expressed in ppb and REEs expressed in ppt. Related to major and trace elements, the minimum value of the majority of the elements (Li, Be, Na, Ca, V, Cr, Mn, Fe, Co, Ni, Zn, Ga, As, Se, Rb, Sr) are in the wheat flour "00" type and in the wheat flour "0" type (B, Na, Mg, Al, Cu, Ag, Cd, In, Cs, Pb, Bi).

On the opposite, the maximum value of these elements is founded in whole wheat flour (B, Mg, K, Ca, Mn, Zn, Ga, Rb, Sr, Ba) and also in the wheat flour "0" type (Na, Al, V, Cr, Fe, Co, Ni, As).

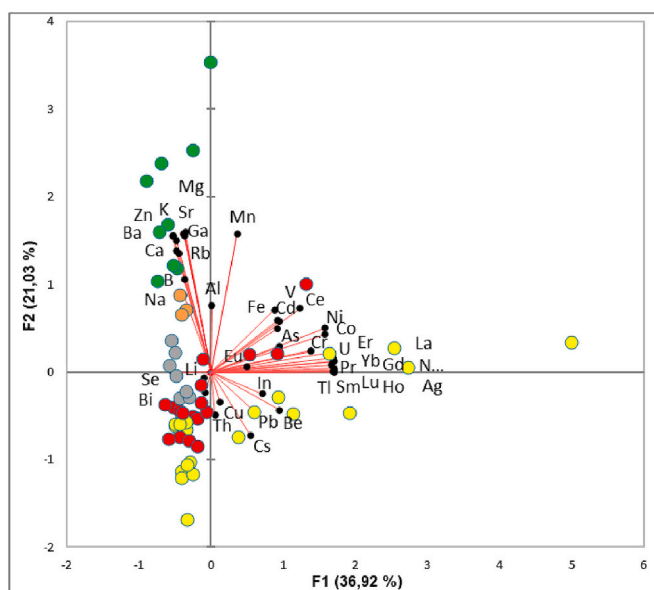


Fig. 1. Biplot obtained using the XLSTAT software by Addinsoft. In red the active variables and with colored circles the samples: wheat flour "00" type in yellow, wheat flour "0" type in red, wheat flour "1" type in gray, wheat flour "2" type in orange and whole wheat flour in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.3.1. Major element data

In detail, potassium is the major element present (as described, for example, by Ekholm et al., 2007 for wheat from Finland; Laursen et al., 2011 for wheat from Denmark and Huang, Zhou, Sun, & Zhao, 2008 for wheat from China) with the highest value of 227.45 ppm in the whole wheat flour followed by magnesium, sodium, calcium, and aluminum, but in much lower ranges than potassium (Table 3).

Potassium shows the highest value respect to the all the other elements in all the different type of flour analyzed and the highest value of 227.45 ppm is related to the whole wheat flour samples. Other research work highlighted the highest value of potassium in whole wheat flour respect to other wheat flour, for example Ertl and Goessler (2018) founded for whole flour much higher potassium concentrations than other flour samples.

Magnesium concentrations range from 4.62 ppm in wheat flour 0 to 54.95 ppm in whole wheat flour (Table 3). Similar values are reported in literature with concentrations, for example, around 12 ppm for wheat crop from south America (Podio et al., 2013) and 1.4 ppm in wheat from Nigeria (Ahmed et al., 2010).

Sodium concentrations is present on average at a quarter of the concentration of magnesium: sodium 5.78 ppm respect to 19.83 ppm of magnesium (Table 3). The highest observed concentration around 11 ppm is related to wheat flour "0" type, which would make grains dietary favorable, when not considering the addition of salt during processing or cooking (Ertl & Goessler, 2018). Higher sodium concentrations in grains around 20 ppm was observed in different area of Argentina (Bermudez, Jasan, Plá, & Pignata, 2011) and in south America (Podio et al., 2013) and from 5 to 16 ppm in *Triticum species* studied by Suchowilska, Wiwart, Kandler, and Krska (2012).

Calcium is together with potassium and magnesium one of the main elements present in grains, but in the flour analyzed the data obtained on calcium is less than the other two elements. Fortunately, the overall range from 1.2 ppm for wheat flour "00" type to 3.8 ppm for whole wheat flour (Table 3) is in agreement with literature data previously described (Ahmed et al., 2010; Ertl & Goessler, 2018; Podio et al., 2013; Suchowilska et al., 2012).

Aluminum shows the lower value, and it is in the range from 0.52 ppm to 9.45 ppm both analyzed in wheat flour "0" samples (Table 3). The values obtained is in good agreement with literature data published by Ertl and Goessler (2018), whose values range between 0.45 and 9.7 ppm. Other data compared to these values are reported, for example, by Ekholm et al. (2007), Vrček and Vinković Vrček (2012) and Podio et al. (2013).

3.3.2. Metal and trace element data

With a range from 0.12 ppm in the wheat flour "00" type to 11.84 ppm in the wheat flour "0" type (Table 3), iron value is the highest of the elements. The values obtained are the same of those from literature, around 23 ppm in flour from Austria (Ertl & Goessler, 2018). Other literature data show value higher compared to this: for example, wheat from Nigeria analyzed by Ahmed et al. (2010) and wheat from Argentina calculated by Bermudez et al. (2011).

As for potassium, manganese shows the lowest value for wheat flour "0" type (4.63 ppm) and the highest value for whole wheat flour (54.95 ppm) (Table 3), indicating high variations between the different kind of refinery. This high variation is previously noted by Akinyele and Shokunbi (2015) and Ertl and Goessler (2018).

Chromium in Table 3 shows a high variability between the minimum value of 0.003 ppm in wheat flour "00" type and the maximum value of 4.33 ppm in wheat flour "0" type, which is a high value compared to those in literature (Ertl & Goessler, 2018; Huang et al., 2008; Nardi et al., 2009 and Vrček & Vinković Vrček, 2012).

The same trend is followed by Cobalt with a minimum value of 0.06 ppb in wheat flour "00" type and a maximum value of 0.10 ppm in wheat flour "0" type (Table 3), which is similar to those present in literature as for chromium, but lower respect to Nardi et al., 2009.

Table 3
Minimum and maximum value and average concentration of the major and trace elements and REEs expressed in ppb. The analytes were analyzed in Elio mode, the analyte with * were analyzed in No gas mode. n.d. means not detected.

Analyte	wheat flour 00			wheat flour 0			wheat flour 1			wheat flour 2			whole wheat flour		
	min	max	average	min	max	average	min	max	average	min	max	average	min	max	average
Li	n.d.	n.d.	n.d.	n.d.	3.77	1.37	0.21	3.98	1.36	n.d.	0.84	0.84	n.d.	0.21	0.11
Be*	0.10	1.04	0.47	n.d.	0.21	0.10	n.d.	0.73	0.23	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
B*	5.60	18.68	13.72	3.32	12.87	8.73	6.43	18.68	14.26	17.85	20.13	18.68	19.09	27.81	22.27
Na	3379.26	5528.56	4786.12	4451.55	10,978.75	5704.24	4951.68	7146.88	5934.77	4983.95	5267.31	5118.05	4940.19	8119.62	7346.35
Mg	4754.70	12,456.61	9370.25	4627.71	13,908.51	11,027.29	9926.98	24,119.49	16,055.68	17,289.83	28,093.94	21,988.52	30,605.70	54,955.09	40,724.04
Al	614.62	2758.31	1016.64	518.59	9450.23	1435.30	801.12	3768.94	1268.59	1080.58	1860.67	1385.31	767.79	6710.14	2672.02
K	61,394.17	88,393.25	74,526.17	57,295.94	98,704.54	80,548.30	57,811.42	142,626.82	99,891.73	117,096.45	147,122.94	127,508.90	162,636.16	227,447.87	188,145.89
Ca	1201.19	2528.55	2058.87	1606.79	2791.78	2273.17	1779.19	2740.32	2302.24	2575.69	3295.13	2880.58	2297.27	3779.66	3118.53
V	n.d.	14.62	2.76	0.21	23.84	4.55	0.35	2.89	1.94	0.18	0.53	0.31	0.10	11.07	3.10
Cr	3.27	2471.45	359.43	37.67	4330.92	813.93	42.99	521.93	332.30	12.89	18.95	14.95	11.39	1585.51	434.10
Mn	77.07	671.14	214.66	102.64	672.92	250.61	207.50	481.92	312.53	249.32	596.04	441.37	503.25	951.67	731.58
Fe	122.19	7719.75	1216.36	304.17	11,840.52	2459.92	501.21	1668.74	1199.12	425.96	585.93	516.31	573.29	6611.97	2244.61
Co	0.06	101.20	17.39	0.58	109.04	19.41	0.37	10.40	6.09	0.33	0.61	0.47	0.45	8.56	2.61
Ni	5.10	3762.72	650.81	26.01	3918.85	711.07	15.55	385.78	228.92	10.87	15.29	13.09	15.16	328.50	102.99
Cu	40.36	266.86	132.02	30.86	94.20	47.23	35.70	62.30	49.51	57.70	71.16	65.94	70.21	97.88	84.14
Zn	85.82	218.18	155.52	91.98	349.50	191.60	149.04	346.93	256.77	270.46	427.97	375.34	362.19	762.02	527.11
Ga	6.21	23.79	15.55	11.52	25.84	15.83	16.14	31.45	20.90	19.46	35.36	26.35	28.59	85.70	44.43
As	0.42	15.38	5.28	0.70	26.18	7.35	2.53	10.74	7.17	1.93	5.34	3.13	1.46	10.09	3.91
Se	n.d.	8.78	4.38	1.25	11.99	6.24	4.60	11.71	7.86	1.53	13.10	6.18	3.48	9.06	5.50
Rb	40.02	111.72	69.37	58.09	141.60	87.72	95.55	207.26	139.25	134.35	193.91	169.15	119.96	355.55	212.08
Sr	20.64	64.38	44.26	36.28	74.63	52.48	58.12	137.30	90.12	97.04	126.75	109.74	88.59	240.01	146.54
Ag	0.04	0.41	0.11	0.02	0.13	0.06	0.04	0.07	0.05	0.05	0.06	0.06	0.04	0.12	0.06
Cd	0.22	1.23	0.59	0.19	0.73	0.47	0.21	0.54	0.40	0.36	1.09	0.72	0.33	0.99	0.66
In	1.13	10.28	4.73	0.63	15.22	5.73	2.85	15.69	6.39	4.02	7.72	5.39	0.85	4.51	2.40
Cs	0.30	17.18	6.35	0.04	0.80	0.28	0.48	9.31	3.10	1.40	4.56	2.49	0.04	2.28	0.53
Ba	26.46	83.30	58.57	47.13	104.03	67.35	59.47	127.66	83.55	88.65	152.26	112.92	123.38	380.91	195.30
Pb	1.79	17.55	4.67	0.54	12.06	2.23	0.66	2.77	1.68	2.52	5.29	3.53	0.62	2.09	1.28
Bi	0.02	0.80	0.36	n.d.	n.d.	n.d.	0.39	4.62	1.56	0.75	0.75	0.75	n.d.	n.d.	n.d.

	wheat flour 00			wheat flour 0			wheat flour 1			wheat flour 2			whole wheat flour		
	min	max	average	min	max	Average	min	max	average	min	max	average	min	max	average
La*	0.024	0.507	0.126	0.027	0.209	0.066	0.031	0.088	0.051	0.056	0.082	0.065	0.040	0.231	0.092
Ce*	0.044	0.614	0.169	0.056	0.357	0.126	0.058	0.190	0.108	0.114	0.214	0.148	0.081	0.535	0.186
Pr*	0.003	0.450	0.091	0.004	0.073	0.021	0.009	0.023	0.014	0.012	0.025	0.017	0.007	0.060	0.021
Nd*	0.009	0.507	0.113	0.015	0.156	0.052	0.023	0.091	0.050	0.043	0.105	0.066	0.027	0.242	0.082
Sm*	0.002	0.466	0.091	0.003	0.072	0.020	0.007	0.023	0.014	0.010	0.029	0.017	0.008	0.060	0.020
Eu*	0.009	0.450	0.103	0.012	0.809	0.140	0.019	1.013	0.188	0.031	0.078	0.048	0.032	0.103	0.058
Gd*	0.005	0.472	0.094	0.007	0.077	0.023	0.009	0.030	0.017	0.011	0.031	0.019	0.011	0.072	0.026
Ho*	0.000	0.452	0.085	0.000	0.067	0.012	0.002	0.004	0.003	0.002	0.004	0.002	0.001	0.009	0.004
Er*	0.001	0.456	0.087	0.001	0.066	0.014	0.003	0.010	0.006	0.003	0.009	0.005	0.002	0.021	0.007
Yb*	0.002	0.443	0.086	0.001	0.070	0.013	0.003	0.006	0.005	0.004	0.007	0.005	0.002	0.016	0.005
Lu*	n.d.	0.459	0.100	n.d.	0.069	0.012	0.000	0.004	0.002	0.000	0.001	0.001	0.001	0.004	0.002
Tl*	0.001	0.415	0.083	0.001	0.061	0.010	0.003	0.005	0.004	0.002	0.005	0.003	0.002	0.011	0.004
Th*	0.013	0.822	0.094	0.005	0.260	0.040	0.027	0.128	0.045	0.020	0.025	0.022	0.020	0.027	0.025
U*	0.020	0.458	0.100	0.005	0.074	0.018	0.008	0.013	0.011	0.021	0.074	0.049	0.015	0.064	0.025

Like for several other elements, zinc concentrations are higher in whole wheat flour than in the other flour, as described by Ertl and Goessler (2018). This is an important factor to take into consideration in people's diets. Anyway, the values are similar to those in other research work previously described.

Compared to other elements, copper concentrations are within a range from 0.03 ppm in the wheat flour "0" type to 0.26 ppm in wheat flour "00" type (Table 3), which are lower than those published in literature (for example by Nardi et al., 2009; Ahmed et al., 2010; and Bermudez et al., 2011).

Rubidium and strontium show large variations from one specimen to another. The values are similar to those compared with literature data: from 0.04 ppm to 0.35 ppm and from 0.02 ppm to 0.24 for Rb and Sr respectively (Table 3). The values are similar to those published by Suchowilska et al. (2012), Podio et al. (2013) and Ertl and Goessler (2018). Both for Rb and Sr the lower value is related to wheat flour "00" type, on the opposite the higher value is related to whole wheat flour.

3.3.3. Contaminants: As, Cd, Ni and Pb

Based on the Commission Regulation (EC) No. 466/2001 (European Commission, 2001) on wheat grains, the mean concentrations of As, Cd, Ni and Pb were below the tolerance limits.

Literature data show arsenic value higher than the concentrations analyzed in this study (0.005 ppm – Table 3) (Huang et al., 2008; Nardi et al., 2009), but similar to those reported by Vrček and Vinković Vrček (2012) and Ertl and Goessler (2018).

The values of cadmium are similar to each other in the different samples, ranging between 0.0002 in wheat flour "0" type to 0.0012 in wheat flour "00" type (Table 3), lower respect to those published by Pruvot, Douay, Hervé, and Waterlot (2006), Lavado, Rodríguez, Alvarez, Taboada, and Zubillaga (2007), Duoay, Roussel, Pruvot, and Waterlot (2008), Chandra et al. (2009); Nardi et al. (2009) and Kirchmann, Mattsson, and Eriksson (2009).

The concentration of Nickel is very different between the different kind of flour samples. The range is from 0.005 ppm in the wheat flour "00" samples to 3.918 ppm in the wheat flour "0" samples (Table 3). In literature, flour values are similar to those calculated in this work: the less value is similar to those published by Nardi et al. (2009) and also by Bermudez et al. (2011) and the highest value is similar to others (for example Ekholm et al., 2007; Huang et al., 2008; Vrček & Vinković Vrček, 2012).

Finally, also lead is under the European limit, ranging between 0.0005 ppm for wheat flour "0" type to 0.0175 ppm for wheat flour "00" type. The results are comparable to those published by Kirchmann et al. (2009), Bermudez et al. (2011) and Ertl and Goessler (2018), but lower than others (Chandra et al., 2009; Duoay et al., 2008; Lavado et al., 2007; Nardi et al., 2009; Pruvot et al., 2006).

3.3.4. REEs

Wheat flour "00" samples present the minimum and maximum value of all the REEs (Table 3).

All the REE elements show value similar to each other, but not under the detection limits as, instead, for the published work in literature (Al-Dayel & Al-Kahtani, 2002; Balaji et al., 2000; Bermudez et al., 2011; Kabata-Pendias, 2010; Kucera, Mizera, Randa, & Vávrová, 2007).

This is a very important result, because having a triple quadrupole mass spectrometer located in a clean room allows to analyze elements present in very low concentrations, which other instruments (or even the same ones, but not in a clean room) are unable to analyze because the values are too close to the detection limit of the instrument.

There are not a lot of recent publications in literature on the use of REEs as traceability markers in flours. Ming and Bing (1998) analyzed REEs in a wheat flour reference materials but not in environmental samples. Jiang, Yang, Zhang, and Yang (2012) characterized 16 Rare Earth Elements in the major foods of China, including cereals, but not flours and much research is based on the use of REEs to identify human

dietary intake.

While REEs are studied a lot in mushrooms (Mędyk & Falandysz, 2022), in wine (Cerutti et al., 2022), and many others.

Following this, it is important to focus on this aspect, because REEs can provide information both on food traceability, but also specifically on bioconcentration and distribution processes.

3.4. Presence of elements as a function of milling

The majority of the elements follow a well-defined trend depending on the degree of refinement of the flour. The quantity of these elements, as clearly visible in the graph of Fig. 2, increases as the refinement of the flour decreases, i.e., from type "00" to "0", "1", "2" and whole wheat.

The graph in Fig. 2 shows a similar trend especially for the major and trace elements (Fig. 2a and b) increasing concentrations as the flour refinement decreases.

Fig. 2b highlight the presence of rubidium, strontium and also barium, followed by the other elements. All of these, except for As, Se and In, increase their concentration following the refinery of the flour.

Regarding the heavy metals (Fig. 2c) the trend is not the same for all the elements analyzed. Mn, Zn and also Cu seem to follow the trend of the refinery of the flour from "00" type to whole wheat, but for the other, especially for Fe, Cr and Ni the trend is different (Table 3).

Generally, the trend following the refinery of the flour is due to the fact that most of these elements are present in the external part of the caryopsis, in particular in the part called bran. The latter is totally present in whole wheat flours, which in fact have maximum values of the selected elements, while it is progressively removed during subsequent processing which increases the degree of milling. This causes a decrease in the concentration of the elements, precisely caused by the removal of the part of the caryopsis that contains them (Ertl & Goessler, 2018).

The opposite trend is observed in the REE diagram (Fig. 2d). Except for Ce and Eu, all the other elements are highly present in the wheat "00" type respect to the other refined flour samples. In this case the trend seems to be "00", "0" or whole, "2" and "1", so not depending on the refinery grade of the flour.

3.5. Soil identification markers as a function of milling

Rb and K and Sr and Ca have geochemical affinity to each other; thus, they can be transferred from the soil to the plant replacing themselves. It is important to note that, while Ca and K are essential elements for the life of the plant, Sr and Rb have no important role (Kabata-Pendias, 2010). Despite this, Rb and Sr can be considered markers of K and Ca respectively, transferred from the soil to the plant.

As far as we know, there are no previous studies using K/Rb and Ca/Sr ratios as tracers of the geographical origin of wheat samples, except for Podio et al. (2013), that showed a different profile in the three studied regions of Brazil. They underline that the composition of the soils based on Ca/Sr and Rb/K ratio is reflected in the wheat grown in the three different areas analyzed. In our research study, soil composition is not known, but the two graphs in Fig. 3, confirm the close connection between them. K/Rb ratio seems to be the same in each type of flour (or very close to each other), but close to Rb respect to K (Fig. 3a). On the other side, Ca/Sr ratio is different into the type of flour and is similar to the trend of Sr (Fig. 3b).

Unlike Podio et al. (2013) which analyzed only one type of wheat grain flour, in our case, we can also notice differences between the different degrees of milling. Fig. 3a underlines that both K and Rb are concentrated more in whole wheat flour samples, then in wheat flour "2" and "1" types, followed by wheat flour "0" type and least of all in wheat flour "00" samples. Even if the differences are minimal between the different kind of flour samples, it can be noted how both K and Rb follow the refinement of the flour: they are more present in less refined flours and less present in more refined flours, probably because Rb is present in



Fig. 2. Concentration of the elements analyzed by ICP-MS-QQQ depending on the milling of wheat flour: a) major elements expressed in ppb; b) trace elements expressed in ppb; c) heavy metals expressed in ppb; d) REE elements expressed in ppt. The average of each type of flour is represented with different colors: wheat flour “00” type in yellow, wheat flour “0” type in red, wheat flour “1” type in gray, wheat flour “2” type in orange and whole wheat flour in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

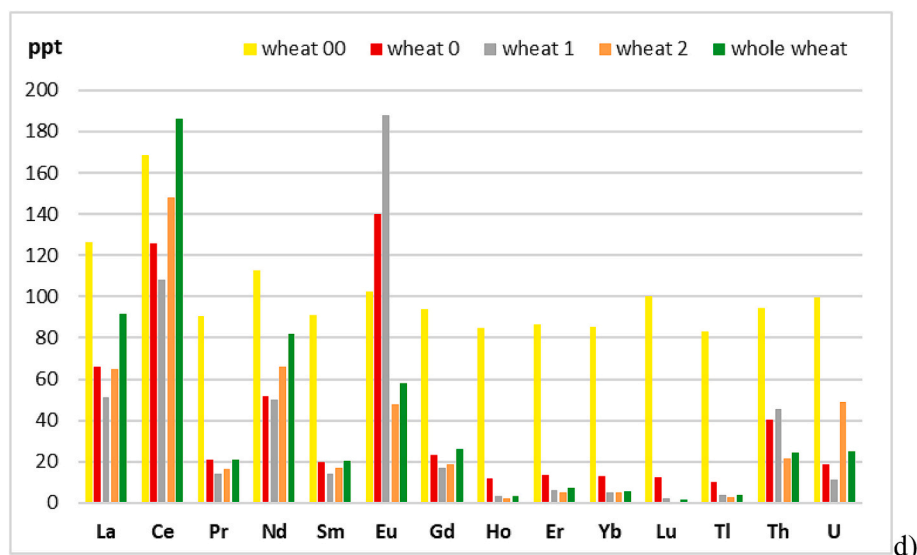


Fig. 2. (continued).

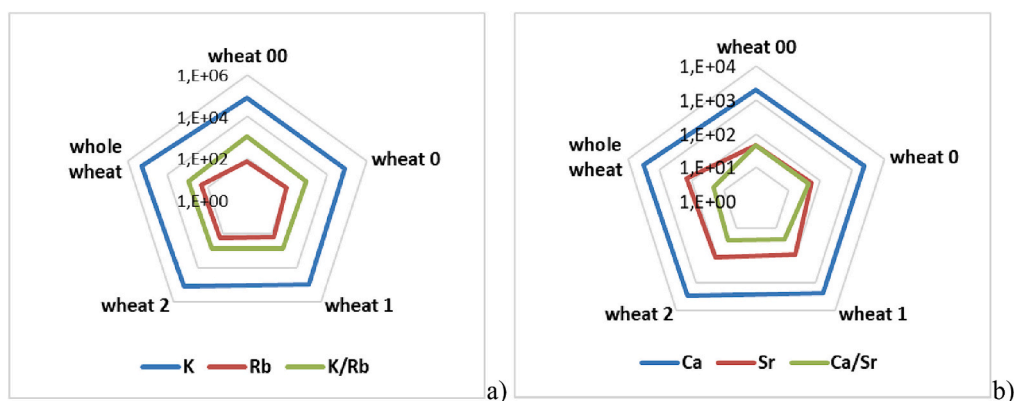


Fig. 3. Spider diagrams of the wheat flour samples on logarithmic scale: a) Potassium concentration (blue), Rubidium concentration (red) and K/Rb ratio (green); b) Calcium concentration (blue), Strontium concentration (red) and Ca/Sr ratio (green). All the elements are expressed in ppb. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the external part of the grain caryopsis and is therefore removed during milling.

The same thing for Ca and Sr (Fig. 3b), although in this case Ca is present in a higher concentration than Sr, because the soil-plant transfer occurs 7.4 times faster for calcium than for strontium (Clauer & Semhi, 2016). Despite this, Ca and Sr also follow the refinement of the flour, reducing their presence with the increase in the degree of refinery. As in the case of Rb, Sr also accumulates in the external part of the caryopsis and is therefore removed during the flour milling phases.

4. Conclusions

This preliminary study focused on the elemental analysis of the different types of wheat flours.

An initial statistical approach made it possible to differentiate the different types of wheat flours based on their degree of milling. The separation between these different types of samples was made on the basis of a part of the elements, in particular trace and REE elements.

The separation between type “0” and “00” wheat flours was not clear, because the elements analyzed do not fall within those discriminating between these two types of flours. The difference between “0” and “00” flours consist, in fact, mainly in the granulometry and not in the presence of trace elements.

The optimization of the methodology both in the sample preparation and in the analysis and the use of a triple quadrupole mass spectrometer in a clean room allowed the detection of elements present in very low concentrations. Values so low that others have not detected.

For this reason, the proposed research methodology can be used in quality control or for the control of possible fraud on the composition or origin of the product, using innovative markers such as REEs, which are already used in other agri-food fields.

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CRediT authorship contribution statement

Chiara Telloli: Data curation, Formal analysis, Methodology, Validation, Visualization, Writing – original draft. **Flavio Cicconi:** Data curation, Formal analysis, Software, Writing – original draft. **Emanuele Manzi:** Data curation, Formal analysis, Investigation, Methodology, Software, Writing – original draft. **Fabio Borgognoni:** Writing – review & editing. **Stefano Salvi:** Formal analysis, Methodology. **Maria Carmela Ipalucci:** Conceptualization, Funding acquisition, Project administration, Writing – review & editing. **Antonietta Rizzo:**

Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Declaration of competing interest

The authors declare no conflict of interest.

Data availability

No data was used for the research described in the article.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2024.139370>.

References

- Ahmed, Y., Landsberger, S., O'Kelly, D., Braisted, J., Gabdo, H., Ewa, I., ... Funtua, I. (2010). Compton suppression method and epithermal NAA in the determination of nutrients and heavy metals in Nigerian food and beverages. *Applied Radiation and Isotopes*, 68, 1909–1914. <https://doi.org/10.1016/j.apradiso.2010.04.016>
- Akinyele, I., & Shokunbi, O. (2015). Concentrations of Mn, Fe, Cu, Zn, Cr, Cd, Pb, Ni in selected Nigerian tubers, legumes and cereals and estimates of the adult daily intakes. *Food Chemistry*, 173, 702–708. <https://doi.org/10.1016/j.foodchem.2014.10.098>
- Al-Dayel, O. A. F., & Al-Kahtani, S. A. (2002). Elemental content in wheat products of AlQuasum region, Saudi Arabia using the INAA technique. *Journal of Radioanalytical and Nuclear Chemistry*, 252, 605–609.
- Andreozzi, C., Rizzo, A., Salvi, S., Bartolomei, P., Telloli, C., Brattich, E., Zappi, A., & Tositti, L. (2023). Self-organizing maps for rare-earth and trace elements profiling of milk samples as a tool to discriminate geographical origins. Available at SSRN <https://ssrn.com/abstract=4386197>.
- Balaji, T., Acharya, R. N., Nair, A. G. C., Reddy, A. V. R., Rao, K. S., Naidu, G. R. K., & Monohar, S. B. (2000). Multielement analysis in cereals and pulses by k α instrumental neutron activation analysis. *Science of the Total Environment*, 253, 75–79. [https://doi.org/10.1016/S0048-9697\(00\)00378-8](https://doi.org/10.1016/S0048-9697(00)00378-8)
- Bermudez, G. M. A., Jasan, R., Plá, R., & Pignata, M. L. (2011). Heavy metal and trace element concentrations in wheat grains: Assessment of potential non-carcinogenic health hazard through their consumption. *Journal of Hazardous Materials*, 193, 264–271. <https://doi.org/10.1016/j.jhazmat.2011.07.058>
- Cerutti, C., Sánchez, R., Sánchez, C., Ardini, F., Grotti, M., & Todolí, J.-L. (2022). Prospect on rare earth elements and metals fingerprint for the geographical discrimination of commercial Spanish wines. *Molecules*, 25, 5602. <https://doi.org/10.3390/molecules25235602>
- Chandra, R., Bharagava, R. N., Yadav, S., & Mohan, D. (2009). Accumulation and distribution of toxic metals in wheat (*Triticum aestivum* L.) and Indian mustard (*Brassica campestris* L.) irrigated with distillery and tannery effluents. *Journal of Hazardous Materials*, 162, 1514–1521. <https://doi.org/10.1016/j.jhazmat.2008.06.040>
- Clauer, N., & Semhi, K. (2016). An evaluation of soil–plant–water interactions based on the $^{87}\text{Sr}/^{86}\text{Sr}$, $1/\text{Sr}$, Ca/Sr , K/Rb and K/Ca ratios of the respective components. *Environmental Earth Sciences*, 75, 690. <https://doi.org/10.1007/s12665-016-5449-0>
- Degree of the Italian Republic President. (2001). *Decreto del Presidente della Repubblica 9 febbraio 2001, n. 187. Regolamento per la revisione della normativa sulla produzione e commercializzazione di sfarinati e paste alimentari, a norma dell'articolo 50 della legge 22 febbraio 1994, n. 146. no. 117. Gazzetta Ufficiale*.
- Duoay, F., Roussel, H., Pruvot, C., & Waterlot, C. (2008). Impact of a smelter closedown on metal contents of wheat cultivated in the neighbourhood. *Environmental Science and Pollution Research*, 15, 162–169. <https://doi.org/10.1065/espr2006.12.366>
- Ekhholm, P., Reinivuo, H., Mattila, P., Pakkala, H., Koponen, J., Happonen, A., Hellström, J., & Ovaskainen, M. (2007). Changes in the mineral and trace element contents of cereals, fruits and vegetables in Finland. *Journal of Food Composition and Analysis*, 20, 487–495. <https://doi.org/10.1016/j.jfca.2007.02.007>
- Ertl, K., & Goessler, W. (2018). Grains, whole flour, white flour and some final goods: An elemental comparison. *European Food Research and Technology*, 244, 2065–2075. <https://doi.org/10.1007/s00217-018-3117-1>
- European Commission. (2001). *Commission Regulation (EC) No. 466/2001. Setting Maximum Levels for Certain Contaminants in Foodstuffs, 2002; US EPA, Risk Assessment Guidance for Superfund, Human Health Evaluation Manual (Part A). Interim Final (vol. I)*. Washington (DC): United States Environmental Protection Agency. EPA/540/1-89/002, 1989.
- European Parliament. (2002). Regulation (EC) no. 178/2002 of the European Parliament and of the council. *Official Journal of the European Communities*, L31, 1–24.
- European Parliament. (2006). Commission regulation (EC) no. 1881/2006 setting maximum levels for certain contaminants in foodstuffs. *Official Journal of the European Communities*, L364, 5–24.
- Fu, Z., & Xi, S. (2020). The effects of heavy metals on human metabolism. *Toxicology Mechanisms and Methods*, 30, 167–176. <https://doi.org/10.1080/15376516.2019.1701594>
- Genchi, G., Sinicropi, M. S., Lauria, G., Carocci, A., & Catalano, A. (2020). The effects of cadmium toxicity. *International Journal of Environmental Research and Public Health*, 17, 3782. <https://doi.org/10.3390/ijerph17113782>
- Huang, M., Zhou, S., Sun, B., & Zhao, Q. (2008). Heavy metals in wheat grain: Assessment of potential health risk for inhabitants in Kun Shan, China. *Science of the Total Environment*, 405, 54–56. <https://doi.org/10.1016/j.scitotenv.2008.07.004>
- Italian Legislation. (1967). *Italian Legislation 580/1967. Disciplina per la lavorazione e commercio dei cereali, degli sfarinati, del pane e delle paste alimentari. no. 189. Gazzetta Ufficiale Serie Generale*.
- Jiang, D. G., Yang, J., Zhang, S., & Yang, D. J. (2012). A survey of 16 rare earth elements in the major foods in China. *Biomedical and Environmental Sciences*, 25, 267–271. <https://doi.org/10.3967/0895-3988.2012.03.003>
- Kabata-Pendias, A. (2010). *In trace elements in soils and plants* (4th ed.). Boca Raton, FL: CRC Press.
- Kirchmann, H., Mattsson, L., & Eriksson, J. (2009). Trace element concentration in wheat grains: Results from the Swedish long-term soil fertility experiments and national monitoring program. *Environmental Geochemistry and Health*, 31, 561–571. <https://doi.org/10.1007/s10653-009-9251-8>
- Kucera, J., Mizera, J., Randa, Z., & Vávrová, M. (2007). Pollution of agricultural crops with lanthanides, thorium and uranium studied by instrumental and radiochemical neutron activation analysis. *Journal of Radioanalytical and Nuclear Chemistry*, 271, 581–587. <https://doi.org/10.1007/s10967-007-0310-2>
- Laursen, K. H., Schjoerring, J. K., Olesen, J. E., Askegaard, M., Halekoh, U., & Husted, S. (2011). Multielemental fingerprinting as a tool for authentication of organic wheat, barley, faba bean, and potato. *Journal of Agricultural and Food Chemistry*, 59, 4385–4396. <https://doi.org/10.1021/jf104928r>
- Lavado, R. S., Rodríguez, M., Alvarez, R., Taboada, M. A., & Zubillaga, M. S. (2007). Transfer of potentially toxic elements from biosolid-treated soils to maize and wheat crops. *Agriculture, Ecosystems & Environment*, 118, 312–318. <https://doi.org/10.1016/j.agee.2006.06.001>
- Ma, C., Xie, P., Yang, J., Liu, F., Hu, H., Du, J., Zhang, K., Lin, L., & Zhang, H. (2022). Relative contribution of environmental medium and internal organs to lead accumulation of wheat grain. *Science of the Total Environment*, 818, Article 151832. <https://doi.org/10.1016/j.scitotenv.2021.151832>
- McCaffrey, R. J., & Lynch, J. K. (2020). Base rates of performance validity test failure among children and young adult litigants with histories of elevated blood lead levels. *Journal of Pediatric Neuropsychology*, 6, 198–202. <https://doi.org/10.1007/s40817-020-00091-6>
- Mędyk, M., & Falandysz, J. (2022). Occurrence, bio-concentration and distribution of rare earth elements in wild mushrooms. *Science of the Total Environment*, 851, Article 158159. <https://doi.org/10.1016/j.scitotenv.2022.158159>
- Ming, Y., & Bing, L. (1998). Determination of rare earth elements in human hair and wheat flour reference materials by inductively coupled plasma mass spectrometry with dry ashing and microwave digestion. This paper was published in the special issue from the BCEIA conference in Shanghai, China, in October 1997.1. *Spectrochimica Acta Part B: Atomic Spectroscopy*, 53, 1447–1454. [https://doi.org/10.1016/S0584-8547\(98\)00159-1](https://doi.org/10.1016/S0584-8547(98)00159-1)
- Nardi, E. P., Evangelista, F. S., Tormen, L., Saint-Pierre, T. D., Curtius, A. J., de Souza, S., & Barbosa, F. (2009). The use of inductively coupled plasma mass spectrometry (ICP-MS) for the determination of toxic and essential elements in different types of food samples. *Food Chemistry*, 112, 727–732. <https://doi.org/10.1016/j.foodchem.2008.06.010>
- Podio, N., Baroni, M., Badini, R., Inga, M., Ostera, H., Cagnoni, M., Gautier, E., García, P., Hoogewerff, J., & Wunderlin, D. (2013). Elemental and isotopic fingerprint of Argentinean wheat. Matching soil, water, and crop composition to differentiate provenance. *Journal of Agricultural and Food Chemistry*, 61, 3763–3773. <https://doi.org/10.1021/jf305258r>
- Poole, N., Donovan, J., & Erenstein, O. (2021). Viewpoint: Agri-nutrition research: Revisiting the contribution of maize and wheat to human nutrition and health. *Food Policy*, 100, Article 101976. <https://doi.org/10.1016/j.foodpol.2020.101976>
- Pruvot, C., Douay, F., Hervé, F., & Waterlot, C. (2006). Heavy metals in soil, crops and grass as a source of human exposure in the former mining areas. *Journal of Soils and Sediments*, 6, 215–220. <https://doi.org/10.1065/jss2006.10.186>
- Raheem, D., Dayoub, M., Birech, R., & Nakiyemba, A. (2021). The contribution of cereal grains to food security and sustainability in Africa: Potential application of UAV in Ghana, Nigeria, Uganda, and Namibia. *Urban Science*, 5, 8. <https://doi.org/10.3390/urbansci5010008>
- Suchowilska, E., Wiwart, M., Kandler, W., & Kraska, R. (2012). A comparison of macro- and microelement concentrations in the whole grain of four Triticum species. *Plant, Soil and Environment*, 58, 141–147. <https://doi.org/10.17221/688/2011-PSE>
- Telloli, C., Tagliavini, S., Passarini, F., Salvi, S., & Rizzo, A. (2023). ICP-MS triple quadrupole as analytical technique to define trace and ultra-trace fingerprint of extra virgin olive oil. *Food Chemistry*, 402, Article 134247. <https://doi.org/10.1016/j.foodchem.2022.134247>
- Vrček, V., & Vinković Vrček, I. (2012). Metals in organic and conventional wheat flours determined by an optimised and validated ICP-MS method. *International Journal of Food Science & Technology*, 47, 1777–1783. <https://doi.org/10.1111/j.1365-2621.2012.03034.x>
- Zwolak, A., Sarzyńska, M., Szyrka, E., & Stawarczyk, K. (2019). Sources of soil pollution by heavy metals and their accumulation in vegetables: A review. *Water, Air, & Soil Pollution*, 230, 164. <https://doi.org/10.1007/s11270-019-4221-y>