

LETTER

Importance of Elemental Chemical Speciation Studies in Enriched Food: Nutritional Quality, Toxicity, and Economic Improvement

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For several reasons, mainly cost and local productivity, the world population does not have access to a balanced diet that contains all the macro and micronutrients necessary to maintain physiological functions for a healthy life. Nutritional education, supplementation, and consuming enriched (or fortified) foods appear as alternatives to supply daily demands and minimize malnutrition. Adding essential elements as salts (e.g., iron, calcium, and zinc) to ready-to-eat processed foods, such as milk, flour, and juices is already adopted in several countries. The choice of the compound to be added, as well as the transport vehicle (foods), must be very well evaluated since the cost, long-term consumption, and bioavailability of the added chemical species are imperative to ensure the nutritional quality of enriched food.¹

Another alternative to produce enriched foods is cultivating an enriched medium (Figure 1), adding essential elements to soil or in nutritive solution (hydroponic procedure), irrigating leaves, or immersing seeds.² In this case, the chemical species used to the enrich food must be absorbed, translocated, and accumulated in the edible part.²

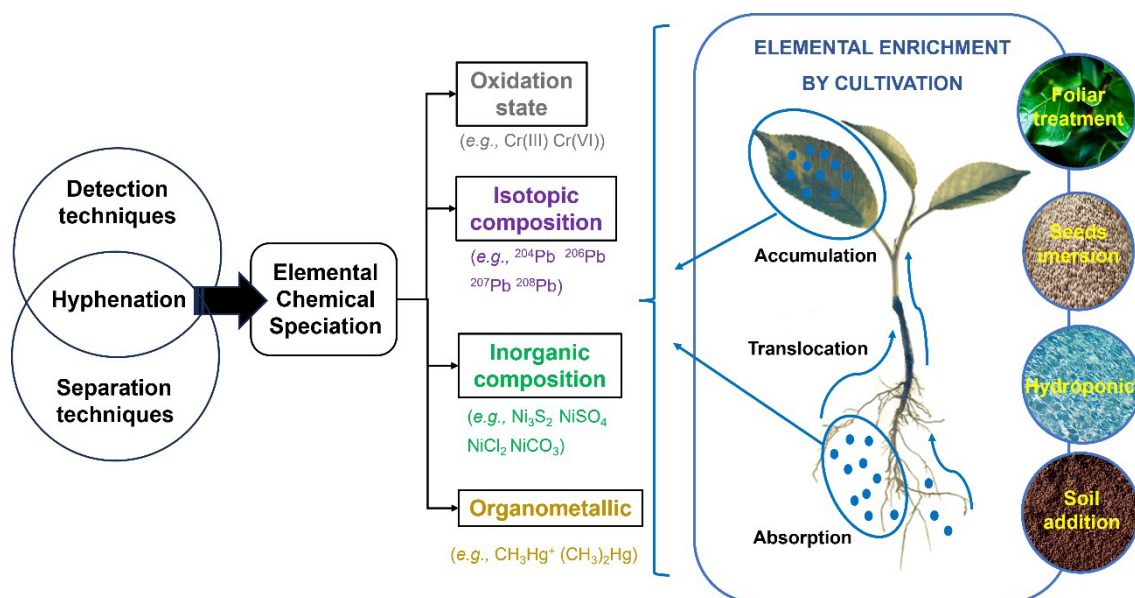


Figure 1. Elemental chemical speciation studies in enriched food.

Studies have shown that the iron enrichment of adzuki beans using iron nitrate or iron chloride was unsuccessful since iron inorganic species interact strongly with the antinutrients (tannins or phytates) present in the roots, forming insoluble complexes and preventing their translocation.³ Alternatives found to overcome this obstacle were enrichment by applying iron complexes with EDTA (ethylenediaminetetraacetic acid)³ or iron nanoparticles, mainly encapsulated.⁴ The nanoparticle application has been gaining prominence in agriculture, aiming to carry fertilizer, pesticides, and nutrients to stimulate plant growth and increase macro and micronutrient availability and absorption efficiency.^{5,6}

Besides the interaction between essential elements with antinutrients, evaluating the competition between elemental species is important, because synergistic or antagonistic effects can be observed. In both cases, chemical species must interact with other components present in food or cultivation medium, altering its chemical composition when compared to food cultivated in conventional conditions. The antagonistic effect between selenium and mercury was observed in edible mushrooms, while the synergistic effect was observed with lead and selenium.^{7,8} Finally, it must be evaluated if the enrichment promotes the production of non-bioavailable or toxic species.

Regardless of the food enrichment strategy, it is important to highlight the need to identify and quantify the elemental chemical species in the enriched foods by chemical speciation analysis. In the Figure 1 is shown examples of elemental chemical species; they can differ according to their oxidation states, inorganic forms, and organometallic or isotopic composition.⁹ For chemical speciation studies, initial fractionation steps (e.g., extraction procedures) are carried out; subsequently, chromatographic, or non-chromatographic methods can be used to identify/determine the chemical species. The hyphenation (Figure 1) between separation techniques, mainly chromatography, with high sensitivity detectors, such as inductively coupled plasma mass spectrometry (ICP-MS), is commonly applied.⁹⁻¹¹ Nonetheless, extremely creative procedures used in non-chromatographic chemical speciation, working only with chemical reactions and solubility differences, can also be applied to determine chemical species. Non-chromatographic strategies were applied for iron (reaction with hydroxylamine and precipitation with trichloroacetic acid and HCl) and selenium (cloud point extraction) speciation in enriched adzuki sprouts.³

In summary, food enrichment success is closely associated with chemical speciation studies since there are chemical species that will be absorbed in a cultivation medium, as well as the chemical species that are formed during translocation and accumulation, which must be in bioavailable forms, in order to act on the different metabolic systems of the human body, including remedying prevalences. In this scenario, it is imperative to go beyond determining the total concentration of essential elements, since quantifying their species will provide information regarding essentiality and toxicity. Finally, the formation of bioavailable chemical species will add nutritional quality and, consequently, economic benefits that are so essential for countries with specific prevalences to combat in a predominantly agricultural economy.

REFERENCES

- (1) Naozuka, J. Elemental Enrichment of Foods: Essentiality and Toxicity. *Nutri. Food Sci. Int. J.* **2018**, 4 (3), 555640. <https://doi.org/10.19080/NFSIJ.2018.04.555640>
- (2) Oliveira, A. P.; Naozuka, J. Enriquecimento Elementar por Meio de Cultivo: Plantas e Cogumelos. *Quim. Nova* **2020**, 43 (9), 1277-1293. <http://dx.doi.org/10.21577/0100-4042.20170601>
- (3) Oliveira, A. P.; Nomura, C. S.; Silva, S. G.; Naozuka, J. Iron and Selenium Speciation in Enriched Adzuki Bean Sprouts after Fractionation Procedures by Graphite Furnace Atomic Absorption Spectrometry. *J. Anal. Pharm. Res.* **2018**, 7 (2), 104–112. <https://doi.org/10.15406/japlr.2018.07.00209>
- (4) Vélez, Y. S. P.; Carrillo-González, R.; González-Chávez, M. C. A. Interaction of Metal Nanoparticles–plants–microorganisms in Agriculture and Soil Remediation. *J. Nanopart. Res.* **2021**, 23 (206), 2-48. <https://doi.org/10.1007/s11051-021-05269-3>
- (5) Arruda, S. C. C.; Silva, A. L. D.; Galazzi, R. M.; Azevedo, R. A.; Arruda, M. A. Z. Nanoparticles Applied to Plant Science: A review. *Talanta* **2015**, 131, 693-705. <https://doi.org/10.1016/j.talanta.2014.08.050>

- (6) Chacón-Madrid, K; Francischini, D. S.; Arruda, M. A. Z. The Role of Silver Nanoparticles Effects in the Homeostasis of Metals in Soybean Cultivation Through Qualitative and Quantitative Laser Ablation Bioimaging. *J. Trace Elem. Med. Biol.* **2023**, 79, 127207. <https://doi.org/10.1016/j.jtemb.2023.127207>
- (7) Oliveira, A. P.; Naozuka, J.; Landero-Figueroa, J. A. The Protective Role of Selenium Against Uptake and Accumulation of Cadmium and Lead in White Oyster (*Pleurotus ostreatus*) and Pink Oyster (*Pleurotus djamor*) Mushrooms, *Food Addit. Contam.: Part A* **2022**, 39 (3), 508-524. <https://doi.org/10.1080/19440049.2022.2026494>
- (8) Oliveira, A. P.; Naozuka, J.; Landero-Figueroa, J. A. Feasibility Study for Mercury Remediation by Selenium Competition in *Pleurotus* Mushrooms *J. Hazard. Mater.* **2023**, 451, 131098. <https://doi.org/10.1016/j.jhazmat.2023.131098>
- (9) Templeton, D. M.; Ariese, F.; Cornelis, R.; Danielsson, L.; Muntau, H.; Van Leeuwen, H. P.; Łobiński, R. Guidelines for Terms Related to Chemical Speciation and Fractionation of Elements. Definitions, Structural Aspects, and Methodological Approaches. (IUPAC Recommendations 2000) *Pure Appl. Chem.* **2000**, 72 (8), 1453–1470, 2000. <https://doi.org/10.1351/pac200072081453>
- (10) Garcia, J. S.; Magalhães, C. S.; Arruda, M. A. Z. Trends in Metal-binding and Metalloprotein Analysis. *Talanta* **2006**, 69 (1), 1-15. <https://doi.org/10.1016/j.talanta.2005.08.041>
- (11) Arruda, M. A. Z.; Jesus, J. R.; Blindauer, C. A.; Stewart, A. J. Speciomics as a Concept Involving Chemical Speciation and Omics. *J. Proteomics.* **2022**, 263, 104615. <https://doi.org/10.1016/j.jprot.2022.104615>



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