



Speciation of challenging elements in food by atomic spectrometry

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ABSTRACT

The review addresses trends in speciation analysis of challenging – rather rarely examined despite their importance for human health – elements in foodstuffs with special attention prior to sample preparation. Elements of interest are cobalt, iodine, manganese, iron, zinc, copper and molybdenum belong to the group of elements still appealed for searching their speciation despite extremely small contents in foodstuffs.

Advantages and weaknesses of recommended procedures are overviewed and discussed, highlighting state-of-the-art speciation methodologies developed so far in the field.

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Contents

1. Introduction	18
2. Microelements of interest	19
3. Analytical problems in the speciation of challenging elements	20
4. Sample preparation – extraction from solid materials	20
5. Isolation from liquid materials	26
6. Analytical procedures	27
7. Conclusions	30
References	30

1. Introduction

Food products contain varying amounts of minerals, and more than 60 elements are typically found in them. Usually, they are classified into two groups: the major salt components and trace elements. The first includes K, Na, Ca, Mg, Cl, S, P and C. Among the trace elements, which are usually present in amounts less than 50 parts per million (ppm), one can find essential nutritive elements (Fe, Cu, I, Co, Mn, Zn, Cr, Ni, Si, F, Mo and Se); nonnutritive but nontoxic elements (Al, B and Sn) and nonnutritive, toxic elements (Hg, Pb, As,

Cd and Sb) [1]. The nutritional value of a food containing a given mineral depends not only on its content, but also on its bioavailability for humans.

The examination of trace element speciation in food is extremely important for understanding the biological activity. Unfortunately, some trace elements are extensively studied, such as Se, As and Hg, while others do not attract the attention of analysts (here, one can find elements discussed in the review). The number of papers concerning speciation of the first mentioned elements in food products have increased significantly and reached a growing rate of 90 papers per year. Elements from the second class of elements, e.g., Co, I, Mn, Fe, Zn, Cu and Mo, have received little attention thus far (Fig. 1). Moreover, many papers apparently offering methods for the examination of their speciation actually describe fractionation procedures, allowing only the classification of an analyte or a group

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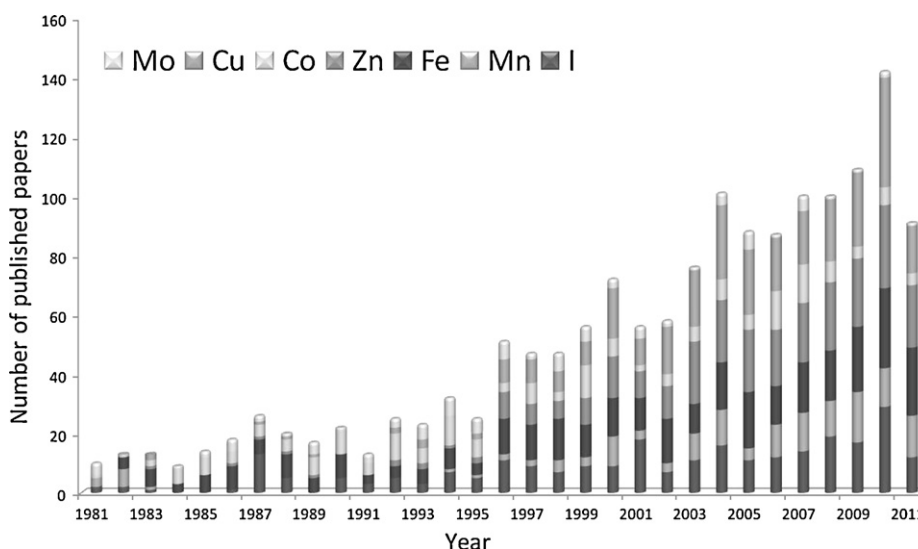


Fig. 1. Evolution of the number of published papers concerning selected elements in food per year from 1981 to 2011. Distribution of research papers as a function of the element considered.

of analytes from certain samples according to physical (e.g., size, solubility) or chemical (e.g., reactivity) properties [2].

The aim of this paper is to present state-of-the-art methods for the analysis of speciation of elements important for human health but belonging to the group of “challenging” elements for analysts.

2. Microelements of interest

Co is an integral part of the only metal-containing vitamin, vitamin B12 [3], which includes a family of compounds containing cobalamin found in meat [hydroxocobalamin (OHCbl) and 5'-deoxy-5'-adenosylcobalamin (AdoCbl, coenzyme B12)] and milk [hydroxocobalamin and methylcobalamin (MeCbl)] products. Other sources of cobalamins are food supplements and fortified foods, which primarily contain cyanocobalamin [4]. Typical levels of cobalamins in food range from 3 to 250 ng g⁻¹, and fortified cereals contain as much as 300 ng g⁻¹ [5]. Knowledge concerning the bioavailability of vitamin B12 from various food sources is rather limited [6], despite its importance for human metabolism, the production of red blood cells and maintenance of the central nervous system.

I, a constituent of the thyroid gland, performs an important function in the synthesis of the thyroid hormones thyroxine (T4) and triiodothyroxine (T3), which are responsible for thermoregulation, metabolism, reproduction, growth and development, blood circulation, and muscle function, as well as the control of the oxidation-to-reduction ratio in cells [7–9].

The recommended dietary allowance (RDA) of I is 150 mg per day in the United States and from 150 to 200 mg per day in European countries [10]. The supplementation of foodstuffs (e.g., iodized salt [11], milk or meat [12]) with I is commonly practiced to prevent I deficiency disorders, although the element is plentiful in the oceans and marine animals. Seaweeds accumulate exceptionally high quantities of I from the sea [13]. The I level in breast milk is known to be affected by the maternal diet, thereby affecting infant nutrition. Infant formula typically must be supplemented with I [14].

The toxicity and bioavailability of I depend on the character of its species. The inorganic forms, iodide and iodate, are less toxic than elemental iodine or some organically bound forms of I [15]. In addition, the bioavailability of organically bound I [moniodotyrosine (MIT) and di-iodotyrosine (DIT)] is less than that of mineral iodide [16].

Fe acts as a cofactor for many enzymes and is involved in oxygen transport and electron transfer [17]. Daily requirements for Fe are 8–18 mg for humans [18], and it is potentially toxic in overdose amounts due to its pro-oxidant activity.

The absorption of iron in humans depends on its oxidation state [19]; ferrous salts are better absorbed than ferric salts, which are poorly soluble in the gut. However, Fe(III) may be reduced to the more soluble Fe(II) form in the gut by the action of gastric hydrochloric acid and reducing agents like ascorbic acid [20]. It is generally accepted that only soluble, non-heme iron can be absorbed [21]. Absorption of Fe from human milk is significantly better than from cow's milk or various infant formulas [22]. Some food components, like phytates, phosphate, polyphenols containing alkyl groups, oxalic acid, casein, phosphoprotein, albumin and minerals, such as Ca, Cu, Zn and Mn, decrease the fractional Fe absorption [23,24].

The form of Fe used for food supplementation significantly determines its uptake by humans. Ferrous sulfate is very well absorbed, but it can be responsible for the discoloration and oxidation of food products. The preferred species of Fe used for the enrichment of flour is the elemental form, which is less likely to change foods [1].

Zn is the activation factor for several enzymes (e.g., carboanhydrase, alkaline phosphatase), it stabilizes the structures of RNA, DNA and ribosomes, and it influences the metabolism of certain hormones, including insulin and gonadotropin [25,26].

The recommended dietary allowance of Zn is 8–11 mg per day, and the tolerable upper intake level (UL) is 40 mg/day, as established by the Institute of Medicine in 2001 [27].

The greatest Zn contents were found in shellfish (approximately 400 ppm). In cereal grains, Zn is found in the range of 30 to 40 ppm. When acidic foods like fruit juices are stored in galvanized containers, an amount of the element sufficient to cause Zn poisoning may be dissolved. In meat, Zn is tightly bound to the myofibrils and has been speculated to influence the water-binding capacity of meat [1].

Cu plays an important role as a cofactor for crucial enzymes [28], including cytochrome c oxidase, Cu/Zn superoxide dismutase and ceruloplasmin, tyrosinase, lysyl oxidase, dopaminemooxygenase and peptidyl glycine a-amidating monooxygenase (required for the modification of neuropeptide hormones) [29].

The recommended dietary allowance for Cu is approximately 1 mg per day, and a range of 1–3 mg is accepted as a safe level of

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