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Review

Review: On published data and methods for selenium in mushrooms

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ABSTRACT

Selected data published on selenium in several species of mushrooms are outlined and discussed in light of performance of analytical methods employed. Data was shown to be either dubious or concentrations too high to be credible and valid in some data reported by authors. Examples of methods and specifically the measurement techniques of Se as reported by authors studying mushrooms are outlined. Also examples of valid and incorrect data on Se in a given mushroom species with data by two or more analytical methods are illustrated. Excessive values reported due to selection of improper method of determination of Se in mushrooms relate largely to improper use of flame atomic absorption spectroscopy (AAS) and inductively coupled plasma – atomic emission spectroscopy (ICP-AES). The biased analytical data published gave a false picture on the composition and nutritional value of mushrooms with respect to selenium.

Contents

1. Introduction

Selenium is important because it is a micronutrient in human nutrition. Therefore it is a matter of high concern for development of suitable analytical methods to determine both total Se and its organic chemical compounds (Bem, 1981; Suzuki, 2004). Numerous analytical methods have been developed to determine total Se in foods, beverages, body tissues and fluids, and various abiotic environmental materials (Bem, 1981; Foster & Sumar, 1995; Kardos, Zimmer, Coni, Cardi, & Stacchini, 1989; Paiva Oliveira, Gomes Neto, Araújo Nóbrega, Miranda Correia, & Vitoriano Oliveira, 2005; Pyrzyńska, Drzewicz, & Trojanowicz, 1998; and many others). Also Se content in mushrooms has become a focus of study. Only a few wild-grown species examined until now can be considered as hyperaccumulators of Se (Falandysz, 2008; Stijve, Noorloos, Byrne, Slejkovec, & Goessler, 1998).

When studying information on Se mushroom content problems are reports of great concentrations of Se in mushrooms that did contain Se at small concentration and can be considered as non accumulators of this element or have not emerged in seleniferous sites. There is estimated number of around 5.1 million species of

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fungi worldwide and the estimated number of edible macrofungi (mushrooms) is around 2,000, while the number of all macrofungi in Europe is around 15,000 (after Falandysz, & Borovička 2013). The biased analytical data published gave a false picture on the composition and nutritional value of mushrooms with respect to total Se content. The aim of this article is to review and discuss published data on total Se mushroom content reported in scientific literature. This is done in light of the performance of the analytical methods employed by the authors.

The general perception relating to our understanding of the biological role of Se has changed since its discovery in the year 1817. Shortly after its discovery, Se was claimed to be toxic and biologically not useful. Selenium that occurs in elevated concentration in topsoil of seleniferous or polluted areas can be efficiently taken-up by plants (Dumont, Vanhaecke, & Cornelis, 2006). For example, wheat grains and straw from selenoferous belt of Punjab in India contained respectively 89 ± 1 and 26 ± 0 μg/g dry weight, while the reference wheat from grown in low Se soils contained 0.007 ± 0.000 and 0.54 ± 0.01 μg/g dw respectively (Bhatia et al., 2011). Prior to the 1930s, reports showed that forage rich in Se in selenoferous areas west of the Mississippi River in the USA resulted in illness and death of horses due to high Se intake (Hinz, 1999).

The beneficial effects of Se as a micronutrient were first recognised in the 1950s, and the first selenoproteins were discovered in the 1970s (Johnson, Fordyce, & Rayman, 2010). Selenoproteins have great health impact in antioxidant enzymes, e.g. gluthatione peroxydases (Gpx), thioredoxin reductase etc. (Tinggi, 2008). Selenoneine (selenyl-*N*, *N*, *N*-trimethyl-L-histidine) is a non-enzymatic seleno-antioxidant that was identified in marine fish and is considered nutritionally important (Yamashita et al., 2011).

Compared with essential trace elements such as Cu, Mg, Zn etc., the nonmetal Se is needed in a much smaller dose. The current recommended dietary daily intake of Se for humans is 57 μg (range 30–85 μg), with a maximum recommended intake rate of approximately 100–200 μg per day (Jarzyńska & Falandysz, 2011a). These small doses do not mean that it is easy to meet the nutritional needs or even exceed the Se requirement in a normal diet, in fact the opposite is more usual. Particularly good sources of Se in the diet are needed to provide the required amount. Low intake of Se from the diet is a problem (Johnson et al., 2010) but pure cases of Se deficiency resulting in low selenoenzyme activity are rare (Ralston & Raymond, 2010). Consequently, efforts to produce Se-enriched foods, food supplements and medicines are common (Falandysz, 2008; Hong, Bañuelos, Fowler, & Lin, 2011).

Selenium for many reasons remains a challenge to analysts, agronomists, nutritionists, physicians and the public. This chemical element has a high biological potential and its' content in foods is usually small. Also small Se doses are required in human nutrition usually between 1 and 3.3 μg/kg body weight daily. The issues of low intake of Se (deficiency), excessive intake (toxicity), as well as the chemical form of Se taken in and their consequences to health have been raised (Dumont, Vanhaecke, & Cornelis, 2006; Ralston & Raymond, 2010). An adequate method of chemical analysis that results in accurate and precise data is a basic tool at all stages of the determinations for dietary intake estimations. Mushrooms have high variability in content of Se (range from ~0.01 to 370 μg/g dry weight) and some species are specifically rich in this element (Falandysz, 2008; Falandysz et al., 2003; Stijve et al., 1998).

2. Methods and results of total Se determinations in mushrooms

2.1. General

Determination and knowledge of the total Se content of biological materials is usually of primary interest to an investigator. Speciation analysis of Se compounds is of high value but requires highly specialized equipment and facilities (Dumont, Vanhaecke, & Cornelis, 2006). The experience with imprecise or doubtful quality data published on Se in mushrooms shows that even determination of total Se content poses difficulty (Falandysz, 2008 and Falandysz, 2012; Machat, Otruba, & Kanicky, 2002). There are several reasons why the determination of total Se in biological materials might be difficult. First of all, there is no robust and cheap analytical method.

The total Se content in the mushroom is not affected by prolonged storage at room temperature (Stijve et al., 1998). Nevertheless, some of the Se compounds are volatile, and if such volatile species are present, some precautions are necessary during materials collection and storage of samples in order to prevent vaporizations.

Mushrooms collected in the field could be of unique value to researchers and the same materials (samples) need to be used for multi-elemental analyses. Several of the sample preparation methods and instrumental measurement techniques have been applied for the examination of Se in mushrooms. These instrumental techniques include UV–Vis spectrophotometry, gas chromatography, flame atomic-absorption spectroscopy, hydride generation – atomic absorption spectroscopy, hydride generation graphite furnace – atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, inductively coupled plasma mass spectrometry, fluorimetry and neutron activation (Alfthan, 2000; Borovička & Řanda, 2007; Byrne, Dermelj, & Vakselj, 1979; Cava-Montesinos, Luisa Cervera, & Pastor, 2003; Cenci et al., 2010; Cocchi, Vescovi, Petrini, & Petrini, 2006; Costa-Silva, Marques, Matos, Barros, & Nunes, 2011; Falandysz et al., 2007a, 2007b, 2007c; Falandysz et al., 2008a, 2008b; Hedrich, 1988; Jarzyńska, Kojta, Drewnowska, & Falandysz, 2012; Jorhem & Sundström, 1995; Kula, Solak, Uğurlu, Işiloğlu, & Arslan, 2011; Lasota & Kalinowski, 1985; Mandić, Grgić, Grgić, & Trstenjak-Petrović, 1991; Melgar, Alonso, & Garciá, 2009; Michellot, Siobud, Doré, Viel, & Poirier, 1998; Pelkonen, Alfthan, & Järvinen, 2008; Polkowska-Motrenko, Dudek, Chajduk, Sypuła, & Sadowska-Bratek, 2006; Quinche, 1983; Stijve, 1977; Tüzen, Sesli, & Soylak, 2007; Wang & Hou, 2011; Zachara, Borowska, Koper, & Wąsowicz, 1986; Řanda & Kučera, 2004). These techniques mentioned and some results reported by researchers' are discussed below [see Figs 1–9; dark shadowed bars (in red on-line) relate to suspicious results because of highly excessive values reported due to selection of improper method of determination, the empty bars (in white on-line) relate to methods of measurement which can give incorrect result due to low sensitivity or non-specific interferences that are difficult to control; and the light shadowed bars with askew lines (shadowed in bluish on-line) are data that appear to be acceptable and by valid methods].

2.2. Spectrophotometry (SPEC)

One team measured Se in mushrooms using spectrophotometry (Lasota & Kalinowski, 1985). To digest mushrooms they used a mixture of concentrated solution of nitric and perchloric acids (3:1). The Se contents were determined spectrophotometrically at λ 340 nm after reaction of Se with 4-bromo-1,2-diaminobenzene. Selenium concentrations determined by them for Common Chantharelle *Cantharellus cibarius* (Fig. 2), Slippery Jack *Suillus luteus*, Variegated Bolete *Suillus variegatus*, Cow Bolete *Suillus bovinus*, Bay Bolete *Xerocomus badius*, Red Aspen Bolete *Leccinum rufum*, Brown Birch Scaber Stalk *Leccinum scabrum*, and Honey Fungus *Armillaria mellea* appear to be overestimated by one to two orders of magnitude compared to other studies, while that for King Bolete *Boletus edulis* (Fig. 3) but also *Sarcodon imbricatum* and Knight Caps *Tricholoma flavovirens* are within an order of