Review: On published data and methods for selenium in mushrooms

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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

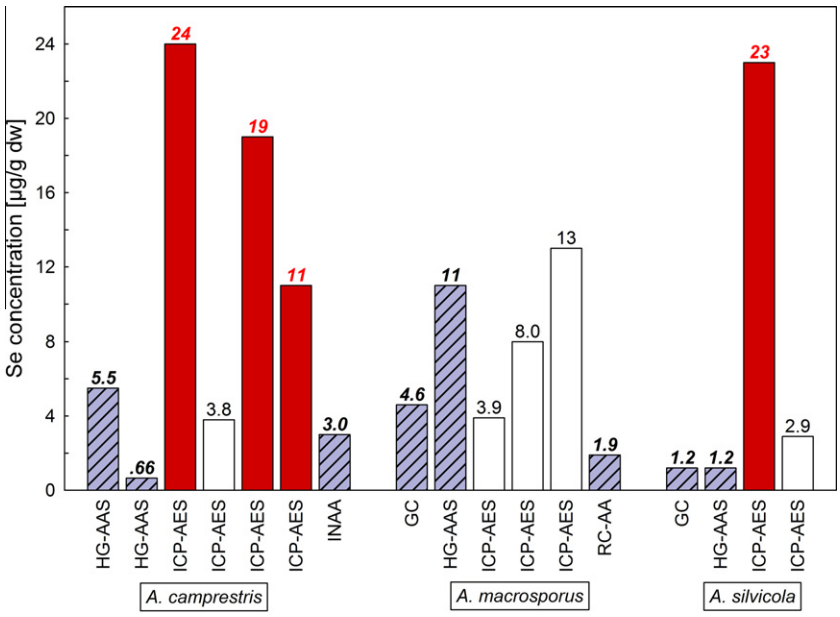

Fig. 1. Selenium in *Agaricus* mushrooms: *Agaricus campestris*, *Agaricus macrosporus* and *Agaricus sylvaticus* (*A. silvicola*) by several authors and techniques (mean values – data adapted from the references cited, respectively).

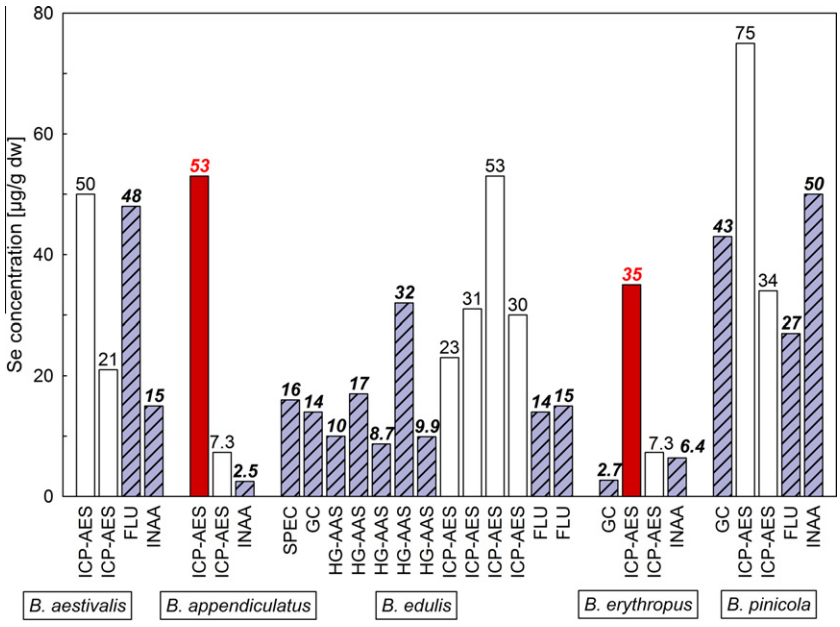

Fig. 2. Selenium in *Boletus* mushrooms: *Boletus reticulatus* (*B. aestivalis*), *Boletus appendiculus*, *Boletus edulis*, *Boletus erythrophus* and *Boletus pinophilus* (*B. pinicola*) by several authors and techniques (mean values – data adapted from the references cited, respectively).

magnitude of those reported using the well validated methods in studies by other researchers (Falandysz, 2008).

2.3. Gas chromatography (GC)

In two separate studies the total Se content was measured using separation by gas chromatography and detection using electron capture detector (GC/ECD) (Quinche, 1983; Stijve, 1977). In a study by Stijve, the mushrooms material was dry-ashed using the oxygen-combustion and the Se oxides were absorbed by hydrochloric acid (Stijve, 1977). Then, Se(VI) was reduced to Se(IV) by heating at 70 °C for 10 min, and derivatized by reaction with 4-bromo-*o*-phenylenediamine to 4-bromo-2,1,3-benzoselenodiazole and the product was extracted with *iso*-octane and subjected to measurement by GC/ECD. In a study by Quinche (1983), the mushrooms were digested with a mixture of concentrated nitric acid (65%) solution and magnesium nitrate, and the Se(IV) was derivatized to volatile 5-nitropiazeselenol that was extracted with toluene and Se was determined by GC/ECD. Both methods with the GC/ECD used in the final measurement gave good comparison with literature (Figs. 1–9).

2.4. Atomic absorption spectroscopy (AAS)

Classical flame AAS techniques suffer from insufficient limits of detection for Se and are not usually used for quantification of this element in biological materials. Nevertheless, selenium was determined by AAS at λ 196.0 nm in mushrooms such as the Vanished

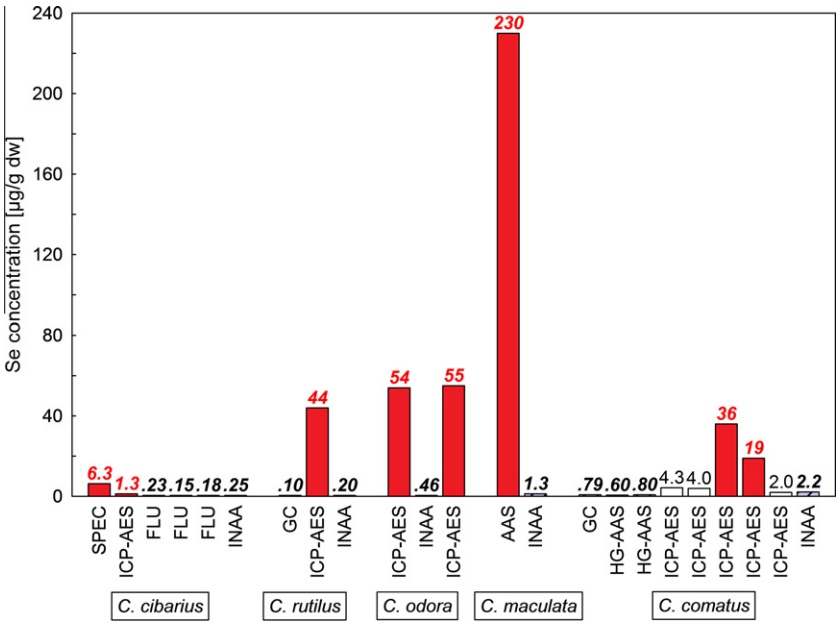

Fig. 3. Selenium in mushrooms such as *Cantharellus cibarius*, *Chroogompus rutilus*, *Clitocybe odora*, *Collybia meculata* and *Coprinus comatus* by several authors and techniques (mean values – data adapted from the references cited, respectively; color figure available online).

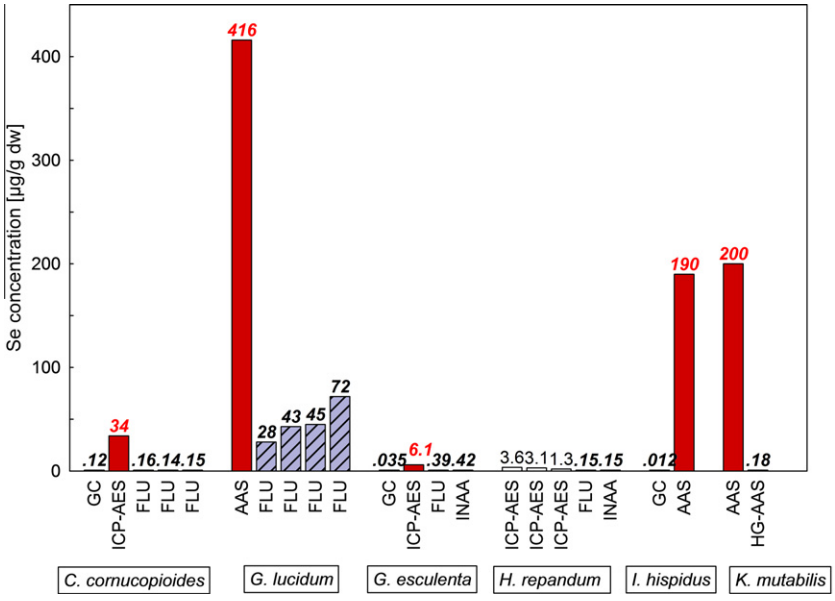

Fig. 4. Selenium in mushrooms such as *Craterellus cornucopioides*, *Ganoderma lucidum* (native/cultivated? but non-Se-enriched specimens by AAS and cultivated Se-enriched specimens by FLU), *Gyromitra esculenta*, *Hydnum repandum*, *Inonotus hispidus* and *Kuehneromyces mutabilis* by several authors and techniques (mean values – data adapted from the references cited, respectively).

Polypore *Ganoderma lucidum*, Orange Caterpillar Fungus or Caterpillar Killer *Cordyceps militaris*, Sheathed Woodtuft *Kuehneromyces mutabilis*, Shaggy Bracket or Shaggy Polypore *Inonotus hispidus* and Spotted Collybia or Spotted Toughshank *Collybia maculata* by direct aspiration of digest (without pre-separation of Se) into flame of AAS (Wang & Hou, 2011). No data on use of certified reference materials are given in that report. Selenium content of *G. lucidum*, *C. militaris*, *K. mutabilis*, *I. hispidus* and *C. maculata* determined by well validated methods by GC is up to 16000-fold less (Stijve, 1977) compared to data reported after the AAS measurement (Figs. 3 and 4).

2.5. Hydride generation atomic absorption spectroscopy (HG AAS)

Determination of the total Se content of foods and other materials by using HG-AAS technique is well established (Cava-Montesinos et al., 2003; Jorhem & Sundström, 1995). The HG-AAS determinations of Se in mushrooms gave data comparable to results by GC and INAA (Figs. 1–9) (Falandysz et al., 2007a, 2007b, 2007c; Falandysz et al., 2008a, 2008b; Hong et al., 2011; Jorhem & Sundström, 1995; Mandić et al., 1991; Stijve et al., 1998).

Mushrooms (usually dried) were treated with a solution of concentrated nitric acid (65%) and further digested with the aid of heat

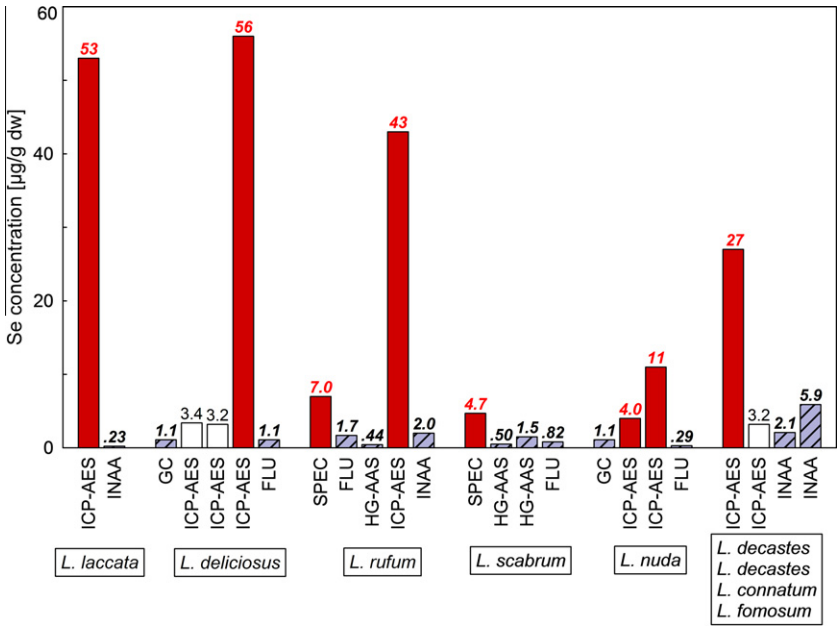

Fig. 5. Selenium in mushrooms such as *Laccaria laccata*, *Lactarius deliciosus*, *Leccinum rufum*, *Leccinum scabrum*, *Lepista nuda*, *Lyophylum decastes*, *Lyophylum connatum* and *Lyophylum fomosum* by several authors and techniques (mean values – data adapted from the references cited, respectively).

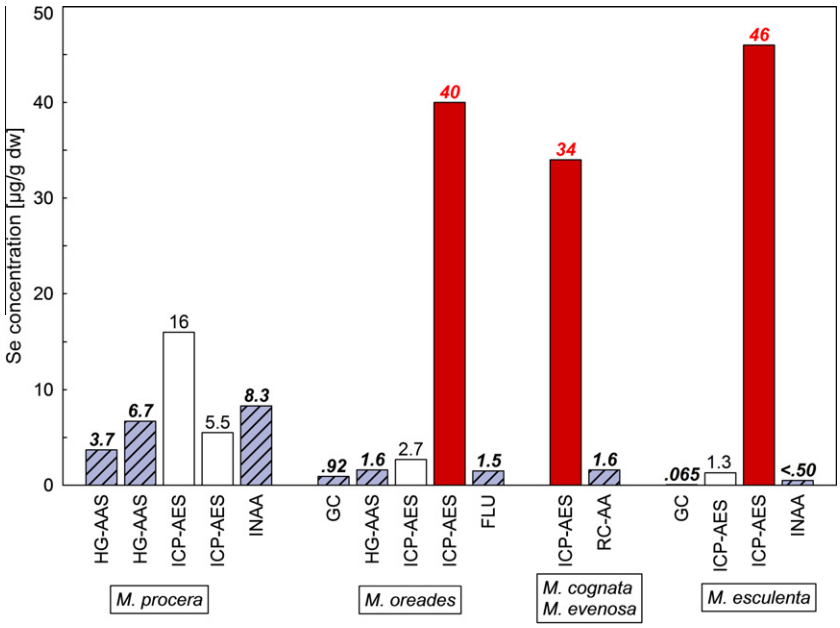

Fig. 6. Selenium in mushrooms such as *Macrolepiota procera*, *Marasmius oreades*, *Melanoleuca cognata, M. evenosa* and *Morchella esculenta* by several authors and techniques (mean values – data adapted from the references cited, respectively).

or microwave energy. The Se(VI) in digested mushrooms is reduced to Se(IV) and then Se(IV) is reduced to the hydride of selenium (H_2Se; selenium hydride) with $NaBH_4$. The selenium hydride formed is separated by volatilization from the oxidised matrix and as the gas is further subjected to measurement by flame AAS.

2.6. Hydride generation graphite furnace atomic absorption spectroscopy (HG GF AAS)

In one study the Se content of mushrooms was determined by HG graphite furnace AAS (Tüzen et al., 2007). Dried mushrooms were microwave digested with a mixture of concentrated nitric acid and hydrogen peroxide solutions. The Se data reported for sixteen species of mushrooms (3 samples per species) collected in Turkey agrees with values reported for the same species collected elsewhere and determined by other studies (Fig. 2) (Falandysz, 2008).

2.7. Inductively coupled plasma atomic emission spectroscopy (ICP-AES/ICP-OES)

The ICP-AES measurement of Se (at λ 196.026 nm or λ 196.027) in biological samples including mushrooms has limitations. The limitations are due to common, non-spectral interferences that

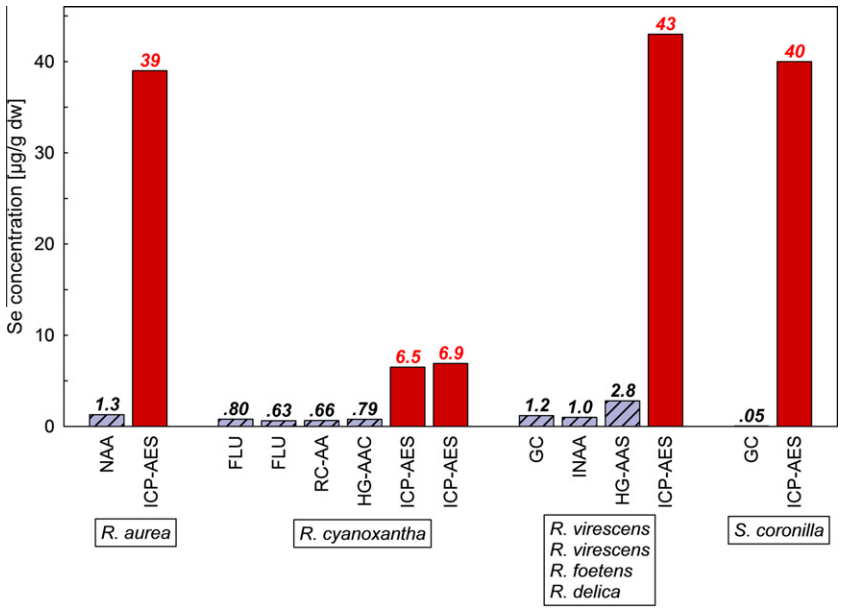

Fig. 7. Selenium in mushrooms such as *Ramaria aurea*, *Russula cyanoxantha*, *Russula virescens*, *Russula foetens*, *Russula delica* and *Stropharia coronilla* by several authors and techniques (mean values – data adapted from the references cited, respectively).

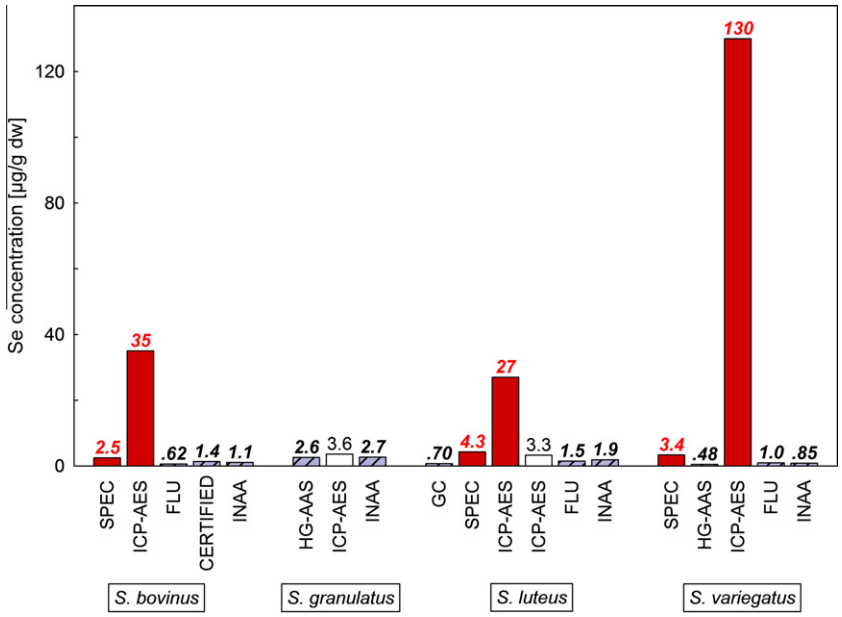

Fig. 8. Selenium in *Suillus* mushrooms: *Suillus bovinus*, *Suillus granulatus*, *Suillus luteus* and *Suillus variegatus* by several authors and techniques (mean values – data adapted from the references cited, respectively).

are difficult to control (Grindla et al., 2007). It was observed recently that Se determination in mushrooms and plant materials by ICP–AES after wet–digestion with nitric acid gives inaccurate and imprecise results and what, most probably, is due to some matrix effect even for well oxidised materials (Jarzyńska et al., 2012). The matrix effects of biological samples due to presence of carbon but also sulfur, phosphorus and bromine cause non–spectral interferences that were observed in the determination of Se by ICP–AES can result in rise of emission signal for Se, and especially when an increasing the amount of carbon is reaching the plasma (Grindla, Mora, Gras, & de Loos–Vollebregt, 2007; Machat et al., 2002). Even if mushrooms or herbs are efficiently digested using concentrated nitric acid (65%) solution, microwaves and pressure and a possible matrix effects from carbon (CO, CO_2) seem negligible, they still can occur and result in biased or imprecise Se data (Jarzyńska et al., 2012). This happens also in Hg measurement in mushrooms by ICP-AES (Jarzyńska & Falandysz, 2011b). It was noted also that if the Se content of mushroom sample is high (>20 µg/g dw), the interferences from a well oxidised sample during the ICP–AES can be negligible (Jarzyńska et al., 2012). Hence, a large variation in Se content in given species of mushrooms, when determined by different authors using ICP-AES, can be because of interference of several agents. This is seen from some of Se data by ICP-AES as illustrated on Figs. 1, 3 and 6, while name of species is of secondary importance. And most difficult to control is the possible formation of interfering carbonyl ions (from CO, CO_2) when digest of different

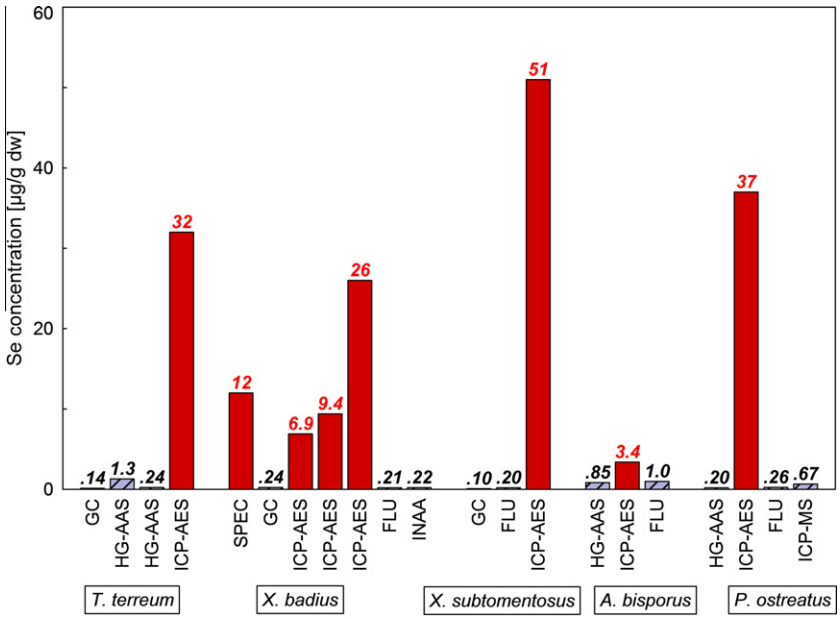

Fig. 9. Selenium in *Tricholoma terreum*, *Xerocomus badius* and *Xerocomus subtomentosus* and in cultivated *Agaricus bisporus* and *Pleurotus ostreatus* by several authors and techniques (mean values – data adapted from the references cited, respectively).

quality is aspirated directly (without pre-separation of Se is aspirated into the plasma of spectrometer. A range of mean values of Se content after ICP-AES are reported in literature and some that are available for the same species of mushrooms are reviewed here – they in figures are indicated by dark shadowed bars (in red on-line) and the empty bars (in white on-line) as illustrated on Figs. 1–9. Certainly, because of reasons discussed above, all such data are suspicious and without doubt sometimes are highly incorrect. It was noted, that even if the mean values of Se in mushroom or plant materials by ICP-AES can be of the same order of magnitude as valid data (obtained by well validated methods), the median values vary highly (Jarzyńska et al., 2012).

If the concentration of Se in mushroom is sufficiently high, i.e. as observed for Upland Horse Mushroom *Agaricus macrosporus* (Fig. 1) as well as for King Bolete *B. edulis* that is rich in Se (Fig. 3), and a spectral signal is strong at λ 196.026 nm and 196.027 nm, the results of Se determined by ICP-AES is in range of values measured by HG-AAS or other credible instrumental techniques. Several authors reported on total Se in mushrooms determined by ICP-AES (Cenci et al., 2010; Cocchi et al., 2006; Kula et al., 2011; Melgar et al., 2009; Michellot et al., 1998). In some of the reports referred certified reference materials were employed (e.g. NIST-SRM 1547 Peach leaves) but this not reflected in quality of Se data in mushrooms and in other reports no such information.

2.8. Inductively coupled plasma mass spectrometry (ICP-MS)

The determination of Se by conventional ICP-MS can suffer from numerous interferences coming from polyatomic ions and single and double charged ions that are formed from components of biological matrices and reagents used (Sucharová, 2011). Measurement of Se by ICP-MS equipped with a collision cell aims to eliminate the interferences mentioned from the signal by Se.

The selenium content of cultivated King Trumpet *Pleurotus eryngi* var. *eryngi* as measured by ICP-MS was <1.5 µg/g dw in control specimens and from 4.6 to 9.3 µg Se/g dw in specimens that emerged in Se-enriched compost (Rodriquez Estrada, Lee, Beelman, Jimenez-Gasco, & Royse, 2009) . Using the ICP-MS measurement, the total Se was also determined in specimens of *Pleurotus florida* cultivated in non-enriched and naturally Se rich composts (wheat straw and grains). The fruiting bodies of *P. florida* from the control study contained total Se at 0.016 ± 0.01 µg/g dw and the specimens that emerged from wheat straw compost naturally rich in Se (from seleniferous belt of Punjab) at 130 ± 2 µg/g dw (Bhatia et al., 2011).

2.9. Fluorimetry (FLU)

In three studies, the contents of Se were determined successfully in several species of mushrooms by fluorimetry (Figs. 2–9). The mushrooms were digested with a mixture of concentrated nitric acid and hydrogen peroxide, concentrated nitric and sulphuric acids; or concentrated nitric and perchloric acids and the Se(VI) was reduced to Se(IV) with hydrochloric acid (Alfthan, 2000; Costa-Silva et al., 2011; Pelkonen et al., 2008; Zachara et al., 1986). A fluorescent derivative of Se(IV) was formed after reaction with 2,3-diaminonaphthalene.

2.10. Instrumental neutron activation analysis (INAA)

The INNA techniques such as radiochemical activation analysis (RC-AA) and neutron activation analysis (NAA) have been respectively used to determine Se content of mushrooms (Borovička & Řanda, 2007; Byrne et al., 1979; Hedrich, 1988; Řanda & Kučera, 2004) . The results on total Se contents of various species of wild grown mushrooms determined by INNA (Figs. 1–8) shows the strength of this approach in determining and confirming Se in their flesh (fruiting bodies) because data gained agree well with those obtained using much cheaper but also reliable Se measurement techniques.

3. Conclusions

A truism is to say that accurate, precise (and relatively cheap) analytical methods are needed when studying Se in any abiotic and biotic matrices. There is estimated number of around 5.1 million species of 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. Data on Se have been published for around 200 species of edible mushrooms and also for a few tens of those inedible to man. These data often refer only to a single or a few specimens from a single site and for around 90% of species there is no valid or any data. Clearly, proper Se measurement techniques have to be used by the authors when they study mushrooms not previously reported for Se content and composition, while the erroneous data and especially for species lacking a wider database need to be improved.

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