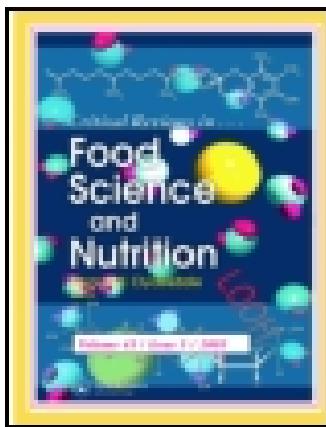


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Publisher: Taylor & Francis

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Critical Reviews in Food Science and Nutrition

Publication details, including instructions for authors and subscription information:
<http://www.tandfonline.com/loi/bfsn20>

"Methods of selenium supplementation. Bioavailability and determination of selenium compounds."

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Accepted author version posted online: 02 Jul 2014.



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To cite this article: Ma?gorzata Bodnar, Marzena Szczyg?owska, Piotr Konieczka & Jacek Namie?nik (2014): "Methods of selenium supplementation. Bioavailability and determination of selenium compounds.", Critical Reviews in Food Science and Nutrition

To link to this article: <http://dx.doi.org/10.1080/10408398.2012.709550>

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“Methods of selenium supplementation. Bioavailability and determination of selenium compounds.”

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Abstract

Selenium, a “dual surface” element, maintains a very thin line between a level of necessity and harmfulness. Because of this, a deficiency or excess of this element in an organism is dangerous and causes health-related problems, both physically and mentally. The main source of selenium is a balanced diet, with a proper selection of meat and plant products. Meanwhile, the proper assimilation of selenium into these products depends on their bioavailability, bioaccessibility, and/or bioactivity of a given selenium compound.

From the time when it was discovered that selenium and its compounds have a significant influence on metabolic processes and in many countries throughout the world, a low quantity of selenium was found in different parts of the environment, pressure was put upon an effective and fast method of supplementing the environment with the help of selenium. This work describes supplementation methods applied with the use of selenium, as well as new ideas for increasing the level of this element in various organisms.

Based on the fact that selenium appears in the environment at trace levels, the determination of total amount of selenium or selenium speciation in a given sample demands the selection of appropriate measurement methods. These methods are most often comprised of a sample preparation technique and/or a separation technique as well as a detection system. The work presents information on the subject of analytical methods used for determining selenium and its compounds as well as examples in literature of their application.

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List of abbreviations:

SELENIUM COMPOUNDS

Abbreviation	Full name in english
(CH ₃) ₂ Se	Dimethyl selenide
(CH ₃) ₃ Se ⁺	Trimethylselenide ion
CH ₃ SeH	Methylselenol
GSH-Px	Glutathione peroxidase
GS-SeH	Glutathionylselenol
GS-Se-SG	Selenodiglutathione
H ₂ Se	Hydrogen selenide
HSePO ₃ ²⁻	Selenophosphate
SeBet	Selenobetaine
SeCys	Selenocysteine
SeCys-tRNA _{UGA}	Selenocysteine and tRNA _{UGA} complex
SeMet	Selenomethionine
SeMSeCys	Selenomethylselenocysteine
SeO ₂	Selenium dioxide, selenium (IV) oxide
SeO ₃ ²⁻	Selenite
SeO ₄ ²⁻	Selenate
Se-sugar-A	Selenosugar A
Se-sugar-B	Selenosugar B
γ-glutamyl-SeMSeCys	γ-glutamyl-selenomethylselenocysteine

ANALYTICAL PROCEDURES

Abbreviation	Full name in english
AAS	Atomic Absorption Spectrometry
AED	Atomic Emission Detector
AFS	Atomic Fluorescence Spectroscopy
CE	Capillary Electrophoresis
CSV	Cathodic Stripping Voltammetry
CT	Cryogenic Trapping
DPCSV	Differential Pulse Cathodic Stripping Voltammetry
DLLME	Dispersive Liquid Liquid Microextraction
ECD	Electron Capture Detector
ESI	Electrospray Ionisation
ET-AAS	Electrothermal Atomic Absorption Spectrometry
EXAFS	Extended X-Ray Absorption Fine Structure
F-AAS	Flame Atomic Absorption Spectrometry
FD	Flame Detector
FID	Flame Ionization Detector
FPD	Flame Photometric Detector
FI	Flow Injection
GC	Gas Chromatography

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GPC	Gel Permeation Chromatography
GF-AAS	Graphite Furnace Atomic Absorption Spectrometry
HSSPME	Headspace Solid-Phase Microextraction
HPLC	High Performance Liquid Chromatography
HG-AAS	Hydride Generation Atomic Absorption Spectrometry
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ICP-OES	Inductively Coupled Plasma Optical Emission Spectroscopy
INAA	Instrumental Neutron Activation Analysis
IEC	Ion Exchange Chromatography
IPC	Ion Par Chromatography
ITP	Isotachophoresis
LA-ICP-MS	Laser Ablation Inductively Coupled Plasma Mass Spectrometry
LC	Liquid Chromatography
LLE	Liquid-Liquid Extraction
LPME	Liquid-Phase Microextraction
LSE	Liquid-Solid Extraction
MW	Microwave
MIP	Microwave Induced Plasma
OES	Optical Emission Spectroscopy
Q-TOF-MS	Quadrupole Time Of Flight Mass Spectrometer
RPC	Reversed-Phase Chromatography
SEC	Size Exclusion Chromatography

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SPE	Solid-Phase Extraction
SPME	Solid-Phase Microextraction
SAX	Stron Anion Exchange
UV	Ultraviolet
UV-VIS	Ultraviolet-Visible Spectroscopic
XAFS	X-Ray Absorption Structure
XANES	X-ray Absorption Near Edge Structure
XRF	X-Ray Fluorescence

1. Introduction

Selenium, the element discovered by Swedish chemist J.J. Berzelius, was initially considered toxic, causing serious illnesses and diseases, especially in animals (alkaline disease or “blind staggers” (Fan and Kizer 1990)). In the middle of the 20th century, the results of disease analysis in rats gave proof of the positive action of selenium but initially only in animals. Twenty years later, the importance of this element in humans was determined after the discovery of the fact that selenocysteine is a central active component of glutathione peroxidase, an enzyme which has antioxidant properties, protecting the organism from the negative actions of “free radicals” by reducing hydrogen peroxide and organic peroxides. The results of the analyses of this fascinating element indicated that it is very easy to exceed the level of requirement to ensure proper function of the organism and attain a harmful level (Dumont et al. 2006). Additionally, selenium content in an organism depends on the chemical form in which the element appears (Gergely et al. 2006a; Ferri et al. 2007). Because of this, a deficiency or excess of selenium in an organism is dangerous and causes health-related problems, both physical and mental. The Recommended Daily Allowance (RDA) of selenium in a properly functioning organism is 55 µg both for women and men (Acu-Cell Nutrition Website). A dose of selenium delivered daily into an organism depends on many factors, mainly on geographic region, meaning diet in a given country. Information on daily consumption of selenium in different countries is presented in Table 1.

The main source of selenium is a proper diet, meaning the right selection of animal and plant products; however, selenium in the food chain assimilates better in plant rather than animal

products (for example, 86% from corn versus 9% from fish) (Wierzbicka et al. 2007). Plants take up inorganic selenium (selenium (IV) and (VI)) from soil and transform it into a more accessible organic form (e.g. selenomethionine or selenocysteine) (Navarro-Alarcon and Cabrera-Vique 2008; Abdulah et al. 2005). Organic selenium is consumed by humans and undergoes changes, during which it joins with protein and amino acids. Selenium delivered during consumption of different food products contributes to the improvement of health through the protection of the immune system, cardiovascular conditioning, proper thyroid function, fertility in men and women, cardiovascular, and above all anti-cancerous function.

2. Selenium in diet

Brazilian nuts (*Bertholletia excelsa*) belong to a group of products most often consumed by residents of South America (Brazil, Peru, Colombia, Venezuela and Ecuador). They are a source of many nutrients such as proteins, phytosterols, tocopherol, magnesium, phosphorous, vitamin E, vitamin B₆, calcium, iron, potassium, zinc and copper (Yang 2009). However, their most characteristic feature is extremely high selenium content, mainly in the form of selenomethionine (Kannamkumarath et al. 2002), thanks to which this product is considered a main source of this element. A diet enriched with this product allows for the obtainment of health benefits, specifically decreasing the risk of the occurrence of chronic illnesses (including the probability of cancer). Results of studies indicated that daily consumption of one nut by patients who are undergoing hemodialysis causes an increase in selenium content as well as activity glutathione peroxidase activity in a human organism, and thus increases its resistance (Stockler-Pinto et al.

2010). According to the United States Food and Drug Administration (FDA): “eating 1.5 ounces per day of most nuts (such as Brazil Nuts) as part of a diet low in saturated fat and cholesterol may reduce the risk of heart disease”.

Brazil nuts are first in a ranking of 10 products containing the largest quantity of selenium. This ranking is presented in Table 2.

3. Bioavailability/bioaccessibility/bioactivity of selenium compounds

Selenium content in a given food product, however, does not mean that the organism will obtain the proper quantity of this element. Proper absorption of selenium from food products depends on:

- bioavailability, meaning a combination of selenium which can be easily transported through the membrane of a biological organism,
- bioaccessibility, meaning the transformation of a given form of selenium within the intestines or lungs into a soluble form, capable of transformation with the biological membrane (Reeder et al. 2006),
- bioactivity, meaning the assimilation of a given form of selenium affecting an increase in the activity of some selenoproteins, such as glutathione peroxidase or iodothyronine deiodinase.

To create metabolic products and to furthermore allow for their use as substrates in various biological processes occurring in living organisms (Fernandez-Martinez and Charlet 2009), the bioactiveness of a given compound or a combination of its bioavailability with bioaccessibility acts as a contributing factor. However, just the bioavailability can contribute to a situation where

selenium compounds are adsorbed on very small colloidal particles that penetrate through the membrane, which leads to the removal of selenium from the body. When a given compound is not bioaccessible for the organism, it “passes through it”, without producing any effect and is ultimately disposed of in the feces (Thiry et al. 2012).

Bioavailability and bioaccessibility depend on physicochemical conditions, such as:

- speciation – the main determinant deciding the “fate” of selenium compounds in the environment; the bioavailability of selenium compounds increases in the following sequence: Se(0) < Se(VI) < Se(IV) < Se(-II) (Fernandez-Martinez and Charlet 2009),
- solubility,
- ionic strength,
- pH,
- redox potential,
- the presence of other metals and substances (e.g. drugs) which may induce synergistic or antagonistic effects.

The bioavailability of selenium in every step of the food chain is very important. A proper form of selenium appearing in a soil conditions its bioavailability to plants. These forms depend on many factors, such as soil type and pH, the presence of other substances in the soil or weather conditions. Plants easily absorb selenium compounds appearing in inorganic combinations, selenite and selenate, which are then metabolized in the tissue and converted into organic forms, among them selenomethionine and selenocysteine. Organic forms of selenium are more bioavailable for animals and humans.

Knowledge on the metabolism of selenium compounds in the human organism, a diagram of which is shown in Figure 1, comes mainly from studies of mice and rats (Rayman et al. 2008). Selenium that reaches a human organism via diet can be either organic or inorganic. Selenomethionine can be directly integrated with proteins, undergo conversion into SeCys (by trans-selenated way) or undergo elimination to CH₃SeH (by α,γ -elimination catalysed by a γ -lyase). SeCys can be integrated into proteins or undergo transformation into H₂Se (by SeCys β -lyase). Selenium can also be delivered into the organism from plant products in the form of SeMSeCys, which is directly metabolized into CH₃SeH (by β -lyase). Inorganic forms of selenium in the organism are subject to changes into H₂Se, a combination of selenium which most likely fulfills a main role in the metabolism. This compound can be converted into:

1. HSePO₃²⁻, which then takes part in the synthesis of selenoprotein,
2. toxic SeO₂,
3. selenosugar A, and then through methylation to selenosugar B, which is excreted from the organism
4. (CH₃)₂Se, a volatile compound excreted from the body through breathing,
5. (CH₃)₃Se⁺, which is excreted via urine,
6. Se-cys-tRNA_{UGA}, which takes part in the synthesis of selenoenzymes.

Regardless of the combination in which selenium appears, it can be incorporated into seleno-dependent proteins during the metabolism process or expelled from body via urine. The fate of selenium compounds in the organism is presented in Figure 2.

The benefits of selenium on the human organism are most often evaluated on the basis of the results of studies of glutathione peroxidase activity or selenium content in biological material (urine, blood, plasma, tissue) (Holben and Smith 1999; Smrkolj et al. 2005). On the other hand, the results of such studies do not deliver information on the anticancerous potential of selenium compounds (Finley 2005b). Therefore, if it is important to ensure the delivery of compounds guaranteeing an increase in the activeness of GSH-PX, the product should contain SeMet, SeCys, selenite and selenate. However, if the supplementation is to be undergone by a person suffering from cancer or who wants to be protected from such an illness, consumed products should contain methylated forms of selenium, such as SeMSeCys or γ -glut-SeMSeCys found in, among others, garlic or broccoli (Finley et al 2005; Finley 2005a).

Bioavailability can be measured on the basis of results of studies conducted *in vitro* or *in vivo*. *In vitro* experiments have many advantages, as they are faster, cheaper, simpler than *in vivo* experiments and they also provide a food estimation. (Pedrero and Madrit 2009).

Studies on humans use a stable isotope of selenium in order to differentiate between selenium originating from food products and selenium from another origin.

In assessing the bioavailability of selenium, it is also important to note the type and temperature of the preparation processes of a given food product. A high temperature can cause the creation of selenium volatile compounds, their decomposition and/or transformation resulting in a decrease of this element in food (Pedrero and Madrit 2009). Examples of products in which the bioavailability of selenium has been reduced as a result of preparation are:

- coffee beans – results of corresponding samples indicate that during the process of roasting, a process occurs in which volatile selenium compounds arise in coffee beans (Meija et al. 2003),
- biscuits with made “biofortified” flour and enriched with selenium; results of studies showed that the main form of selenium is SeMet, and after baking SeMet selenoxide (Kirby et al 2008),
- plants from the *Brassicaceae* family, for example broccoli and radishes, which contain SeMSeCys and after cooking, 85-89% of selenium compounds go into the water in which the plants were cooked (Rayman et al. 2008)
- asparagus, mushrooms, vegetables, dairy products, which show a 40-50% loss of selenium compounds during cooking, especially when salt and vinegar is added (Fordyce 2005).

In summary, selenium content in the organism depends on the bioavailability, the bioaccessibility and/or the bioactivity of selenium compounds contained in food products. The results of many studies indicate that organic selenium compounds, such as SeMet, contain the following characteristics, as compared to inorganic combinations of these compounds (selenite and selenate):

- ✓ better absorption,
- ✓ greater retention,
- ✓ higher accumulation of Se in blood and tissues (Fox et al. 2004)

Furthermore, it is also important to note that organic forms of selenium are better at protecting the body against deficiencies of this element than inorganic forms, which in turn pose a greater risk of toxic symptoms – excessive accumulation of selenium in the body.

Taking into account three types of influence of selenium on the organism, the following combinations of selenium are important:

- ✓ Se accumulation in tissues: SeMet (from Se-yeast) (Rider et al. 2009),
- ✓ increasing GSH-Px activity: selenite or selenate (from meat or fish) (Neve 1995),
- ✓ Se as chemopreventive agent: SeMSeCys and γ -glut-SeMSeCys (from *Brassica* or *Allium* plants) (Ogra et al. 2005).

The discovery of new selenium compounds as well as their function will allow for the analysis of their bioavailability and bioactivity, which will allow for a comparison of their actions against known selenium compounds (Thiry et al. 2012). It is important to conduct speciation studies, whose aim would be to determine individual selenium compounds in samples taken directly from the gastrointestinal tract, which will allow one to predict what forms of selenium (organic and inorganic) are essential for health and human development (Pyrzynska 2009). This will also contribute to an enrichment of knowledge on the subject of different food products which may be recommended by nutritionists and doctors as a natural source allowing for an increase in selenium content in the body, a natural dietary supplement.

4. Supplementation as a way of enriching diet with selenium

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The daily recommended dose of selenium is easily achievable to consumers living in countries such as: the USA, Mexico, Colombia, India or Iceland. Many regions of the world, such as Northern Europe (Finland, Poland, Great Britain), Australia, New Zealand and China (Bitterli et al. 2010) have predominantly selenium-poor soil, which leads to a deficiency of this element in humans. A low content of this element in a diet can be caused by the following factors (Wierzbicka et al. 2007; Navarro-alarcon and Cabrera-Vique 2008; Nyam News):

- 1) low content of selenium in soils,
- 2) acid rain, which lowers the absorption of selenium by plants,
- 3) intensified agricultural production, which contributes to soil erosion,
- 4) consumption of products with a low selenium content,
- 5) decrease of selenium content in a given product caused by pre-treatment of the product, such as cooking, frying, baking bread (40%); losses are caused by the creation of volatile selenium compounds,
- 6) the occurrence of diseases which requires parenteral nutrition,
- 7) the occurrence of metabolic diseases,
- 8) the occurrence of malabsorption syndromes ,
- 9) culinary tastes in various societies.

An appropriate level of selenium in the human body has a significant impact on a person's health and development. The importance of selenium for human health and development was recognized for the first time during investigations of the causes of Keshan and Kasin-Beck diseases, appearing in the northeastern region of China. The results of these studies indicated that

these endemic diseases are related to low selenium content in the organisms of the sick. Results of many studies indicates some other potential beneficial effects of selenium (especially in selenium-dependent proteins) for human health such as (Walpole 2007; SanzAlaejos et al. 2000; Clark et al. 1996; Bleys et al. 2008; Nyman et al. 2004; Rayman 2000; Saxena and Jaiswal 2007; Harman 1996; Orr and Sohal 1994; Virtamo et al. 1985; Arner 2009; Arthur et al. 1991; Kantola et al. 2004; Sinclair 2000; Baum et al. 1997):

- ✓ prevention of certain types of cancer,
- ✓ stimulation of the immune system,
- ✓ detoxification processes,
- ✓ prevention of cell aging,
- ✓ protection of the cardiovascular system,
- ✓ the synthesis of thyroid hormones,
- ✓ protection of male and female fertility,
- ✓ protecting the organism from various viruses (e.g. HIV-1).

Specific role of selenium compounds in above-mentioned processes need to be confirmed in further studies.

5. Selenium supplementation methods

Ever since it was found that selenium has a significant impact on many metabolic processes and many countries around the world have a deficiency of this element, much attention was given to research into effective methods of supplementing the environment with selenium (Arthur 2003). This method should quickly and effectively influence and increase the content of selenium in soil, and in animal and human organisms. It is worth noting that the process of supplementing the

environment with selenium requires special care and should be monitored by appropriate institutions and organizations which have the proper tools, meaning analytical methodologies and control-measuring devices.

5.1. The following “classic” methods of food supplementation can be found in the literature:

5.1.1. Fertilization of soils (enrichment of fertilizers with inorganic selenium compounds)

This method was used for the first time in Finland, where low selenium content was attributed to geochemical and climate-related conditions (Eurola et al. 1990). Low selenium content in the environment resulted in a low daily intake of selenium by humans (0.02-0.03mg) (Koivistoinen 1980). For this reason, since 1984 the enrichment of fertilizers with selenium (VI) sodium has been used, both in the production of grain and feed (Navarro-Alarcon and Cabrera-Vique 2008; Arthur 2003; Hartikainen 2005; Varo et al. 1988). Initially, 16 mg of selenium (VI) sodium/kg of fertilizers was added during the production of cereal products as well as 6 mg of selenium (VI) sodium/kg of fertilizer during the production of feed. This procedure was carefully monitored because of the narrow range between “appropriate” content (beneficially affecting bodily function) and toxic content of this element. After introducing selenium into fertilizers, many studies were conducted which demonstrated a rapid increase in selenium in soils, crops and food products (Varo et al. 1988), among others in flour and bread (Eurola et al. 1990). Selenium content in these products was determined using the ET-AAS technique. Information on the change in selenium content in two types of flour and bread is presented in Figure 3.

The change in selenium content was also noticed during analysis of human milk samples before and after supplementing fertilizers. Results of these studies indicate a significant increase

in the level of selenium content in the milk of nursing mothers and its impact on the reduction of zinc and copper levels in analyzed samples (Kantola and Vartiainen 2001).

The level of selenium determined in blood plasma of Finnish residents increased from 0.7 µmol to 1.4 µmol, regardless of the subjects or region (Arthur 2003). In a comparison of test results before and after the use of supplementation, the content of this element increased 3 to 10-fold. In 1990, the amount of selenium added to all fertilizers was averaged to 6 mg selenium (VI) sodium/kg. However, since 1998, 10 mg selenium (VI) sodium/kg is added to fertilizers. A similar strategy was used in Australia and New Zealand. This procedure, which is subject to continuous monitoring, resulted in an increase in selenium content in various areas of the environment (Arthur 2003).

The reasons for the application of sodium selenate for the enrichment of fertilizer was:

- 1) better bioavailability of inorganic forms of soils for plants, which confirm the results of supplementation studies of tomato crops, strawberries, radishes and cabbage (Carvalho et al. 2003),
- 2) lower price of sodium selenate as compared to organic forms of selenium.

In summary, the addition of sodium selenate to fertilizers causes an increase of this element in both animal and plant products. Consumption of given products by humans leads to an increase in the level of selenium in the organism (Arthur 2003; Alfthan et al. 1991) and thus improves the effectiveness of many healthy metabolic processes.

5.1.2. Pharmacological products – dietary supplements (the addition of organic or inorganic selenium compounds)

Another method of supplementing the level of selenium in the body is the use of appropriate pharmaceuticals or dietary supplements containing selenium. These formulations contain organic selenium, such as selenomethionine or selenoysteine, or inorganic in the form of selenite and selenate. The majority are vitamin and mineral products sold over the counter in pharmacies, herbal stores, drugstores or in grocery stores.

The results of blood samples of residents of regions in China where the soil is poor in selenium indicate an increased level of this element in their blood, after prior supplementation with tablets containing a certain amount of sodium selenite or L-selenomethionine. Additionally, it was found that supplementation is more effective when an organic form of selenium is used (2 times greater bioavailability than with inorganic forms), because L-selenomethionine increases the activeness of glutathione peroxidase activity as well as increases the level of selenium in blood (Xia et al. 2005).

A different approach of dietary supplementation for women was proposed by the inventors of SEL-BRCA1, to protect against the development of breast cancer. The patented product contains selenium in the form of selenite (SeO_3^{2-}), however it lacks methylated forms of selenium (because of their likely uselessness) and SeMet (because of the risk of the appearance of abnormal proteins) in its composition (Sel-BRCA1 Website).

5.1.3. Selenium enriched yeast (containing, above all, organic selenium compounds)

The positive health effects of yeast on a living organism were first recognized in 1957. Results of studies indicated that the so called “factor 3” element, when isolated from yeast, prevents dietary liver necrosis in rats (Schwarz 1951; Schwarz and Foltz 1957). “Factor 3” is most likely selenomethionine, because it is the main natural occurring combination of selenium in yeast.

Selenium enriched yeast is one of the main products which is used to increase daily consumption of this crucial element. The first products containing selenium enriched yeast were introduced into the US market in 1974 (Schrauzer 2006). *Saccharomyces cerevisiae*, or baking or brewers yeast, are able to accumulate even 3 000 µgSe/g, mainly in the form of selenomethionine. Information on the percentage content of SeMet in selenium enriched yeast (Se-yeast) from different manufacturers is present in Figure 4.

SeCys is the second most abundant identified species (2-4% of total Se content). Inorganic selenium (IV) is found to be less than 1% of total Se content. This fact confirms that almost all of the selenium in Se-yeast is organic (EFSA Website).

The bioavailability of selenomethionine contained in yeast is higher (around 1.5-2 times) than the bioavailability of inorganic forms of this element (EFSA Website). This is confirmed by results of studies described in literature (Neve 1995; Alftan et al. 1991, Levander et al. 1983; Clausen and Nielsen 1988; Thomson et al. 1993; Kumpulainen et al. 1985; Yoshida et al. 1999).

The results of relevant studies can be the basis for the finding that inorganic forms of selenium have a greater ability to synthesize GSH-Px; meanwhile, organic forms, such as SeMet, are dominant in their ability to accumulate and incorporate into tissue (Neve 1995).

It was found that the numerical value of the LD₅₀ parameter for selenium-enriched yeast is 37.3 mg/kg, whereas the LD₅₀ for sodium selenate is 12.7 mg/kg (Rayman 2004), which, despite the greater bioavailability of organic forms of selenium, proves that these compounds are less toxic than inorganic forms.

The advantages and disadvantages of using selenium-enriched yeast as a dietary supplement is presented in Table 3.

In 2008, a panel of experts from the European Food Safety Authority (EFSA Website) concluded that: “the use of selenium-enriched yeast (...) as a source of selenium when used in foods for particular nutritional uses and in foods (including food supplements) for the general population does not present a safety concern at the proposed intake levels”.

Dietary supplementation with selenium-enriched yeast is often used in studies of the anti-cancerous properties of this element. In these studies, a dose of 200-300 µg of selenium is most commonly used, which causes an increase in the content of selenium in blood and an increase in the activeness of glutathione peroxidase. The results of these studies can be the basis for the conclusion that dietary supplementation with selenium-enriched yeast does not protect from the “primary endpoint” of different types of cancers; however, it contributes to a reduction in the overall mortality of people with various cancers, particularly prostate cancer, colorectal cancer, as well as skin cancer (basal/squamous cell carcinomas) (Combs Jr et al. 1997; Combs Jr et al. 2001; Hawkes et al. 2008; Robinson et al. 1997; Clark et al. 1998; Clark et al. 1996).

In summary, selenium-enriched yeast is a safe product, which, due to its large bioavailable form of this element – SeMet – as well as having no evidence of toxic effects (even with large daily dose of 300-800 µg) can be a dietary supplement component, which regulates the level of selenium in the human body, the activeness of seleno-dependent proteins, and acts as an anti-cancerous agent (Rayman 2004).

5.2. Asides from “classic” supplementation methods, the following “alternative” methods of supplementing food products with organic selenium compounds may be identified

5.2.1. Selenium-enriched plant biomass – obtained through the germination of seeds of chosen plants (e.g. cereals) in water containing inorganic forms of selenium (Wierzbicka et al. 2007)

It is suspected that methylselenol (CH_3SeH) is the active form of selenium which causes a reduction in certain types of cancer (mammary cancer, prostate cancer, skin cancer) (Abdulah et al. 2005; Whanger 2004). Based on the fact that CH_3SeH is volatile, it is important to know the precursors of this compound, due to which its synthesis in an organism is possible. One such combination is SeMSeCys (Ip 1998), which is directly metabolized into methylselenol, which makes it unique among other compounds which require several steps to synthesize into a volatile Se form. SeMSeCys occurs mainly in selenium-enriched plants from the *Allium* and *Brassica* family, such as broccoli, onions, garlic, and Indian mustard (Finley et al. 2005; Finley 2005a; Pyrzynska 2009; Cai et al. 1995; Seo et al. 2008; Ip et al. 2000; Wrobel et al. 2004; Khakachchi et al. 2004; Montes-Bayon et al. 2002; Arnault and Auger 2006; Roberge et al. 2003). It was noted that research using a synthetic SeMSeCys compound did not yield satisfactory results. Only when plants containing SeMSeCys were used was it concluded that this compound, naturally occurring in plants, has a positive effect on preventing certain harmful processes occurring in the human organism, including cancer (Whanger 2004; Finley et al. 2001; Ip et al. 1992). The results of the above described speciation studies of selenium-enriched plants indicate the significance of their conduct, with special attention paid to the bioavailability of selenium compounds and their participation in healthy processes in the human body (Rayman et al. 2008). It seems that most importantly, attention should be paid to the participation of selenium in cancer prevention, since the discovery of its positive effects could reduce the occurrence of prostate

cancer, breast cancer or colon cancer by up to 50% (Whanger 2004). So far, rats have been used in these types of studies as experimental animals. Their diet was supplemented with various forms of selenium. The results showed that SeMSeCys, when compared with SeMet or sodium selenate, is a more effective source of protection against cancers (chemoprevention) (Ip and Ganther 1990). This fact has contributed to increased interest in studies of the remaining methylated selenium compounds, including methylselenic acid) and selenobetaine, which also demonstrate a likely effect against certain types of cancer (Ip et al. 2000; Dong et al. 2002; Zhao et al. 2003).

5.2.2. A selenium enriched biomass of non-pathogenic microorganisms (lactic acid bacteria of the *Lactobacillus* genus; bacterial starter cultures, meaning yeast propagated in a culture medium containing inorganic sources of selenium) in which the main form of selenium is SeCys (Wierzbicka et al. 2007; Calomme et al. 1995; Andreoni et al. 2000) and can be used for the production of dairy products, such as kefir or yogurt (Alzate et al. 2008).

The above-mentioned methods have been used in the development of technological solutions consisting of fermented food supplementation in organic forms of selenium, through the use of seed germination processes of selected plants and microorganism growth. The following were used in the studies:

- ✓ lactic acid bacteria from the *Lactobacillus* genus,
- ✓ bacterial-baking yeast starter cultures,
- ✓ germinating seeds from select plants.

The results of studies, which demonstrate the ability of selenium's accumulation and bioconversion abilities through research materials (transformation of inorganic forms into organic forms by way of enzymatic transformation), allowed for the development of effective methods of obtaining a plant or microbial selenium-enriched biomass, which can be used in the production of food products (e.g. beer, yogurt or cheese) formed through the fermentation process. In the framework of the INCO-Copernicus project, a production process was developed for bread fermented with selenium-enriched bacteria, starter cultures and plant seedlings. Studies of this bread indicated:

- ✓ the ability of microorganisms to accumulate and biotransform selenium,
- ✓ the presence of selenium in products, mainly in the form of selenomethionine (SeMet),
- ✓ high bioavailability of selenium from products, inferred on the basis of results of studies of people consuming bread enriched with selenium (changes in selenium content in blood and plasma and changes in glutathione peroxidase activity were demonstrated),
- ✓ the effectiveness and efficiency of given dietary supplementation methods (Ambroziak et al. 2007; Diowksz et al. 2007).

Therefore, food products, which are source of selenium for humans, should provide a high bioavailability of selenium (through the use of its appropriate form), and thus meet the rigors of a functional food that provides nutrients and beneficial effects on the health, wellbeing and physical abilities of humans (Reilly 2006).

In summary, selenium supplementation is desirable in areas where selenium intake is relatively low. Among the above-mentioned supplementation methods there are two methods

which are used more frequently: enrichment of fertilizers with inorganic selenium compounds and pharmacological products. Although these methods can effectively increase the level of this element in a living organism, they are limited by some factors such as:

- ✓ bioavailability of selenium from fertilizer supplementation depends on the ability of a plant to take up selenium from soil, selenium metabolism in plants, soil conditions, weather conditions, plant species;
- ✓ bioavailability of selenium from pharmacological products depends on interaction with other micronutrients in the supplement, effects derived from their simultaneous administration with specified medication, timing, dose and schedule of supplementation (Dumont et al. 2006).

Also „alternative” methods of supplementation can be feasible to increase selenium levels in organisms. These methods use selenium enriched yeast, plant biomass and/or biomass of non-pathogenic microorganisms to produce „natural” supplements e.g. Se enriched broccoli, Se enriched onion or Se enriched bread. Bread as a common product, consumed by many individuals, may be a good source of selenium. However these methods need further studies (e.g. stability of selenium compounds under baking or cooking conditions; metabolism of possible chemopreventive agents: SeMSeCys and γ -glut-SeMSeCys) to confirm their usefulness in future.

6. Analytical methods for the determination of selenium

The determination of elements in the environment at trace levels requires the selection of appropriate methods of measurement. The most important aspect of research is the selection of an analytical method, which allows for the determination of the content of a given element or

compound. Most importantly, the following should be considered (Ferri et al. 2007; Hartikainen 2005; Germ and Stibilj 2007; Manjusha et al. 2007; SanzAlaejos et al. 2000; Najafi et al. 2010; Ellis and Salt 2003; Konieczka and Namiesnik 2007):

- ✓ limit of detection, by means of which the smallest content or smallest concentration that is possible to determine in a substance is found using a given method or analytical technique with a specified probability,
- ✓ selectivity of the method, which makes the determination of a given chemical substance possible in the presence of other components in the analyzed sample,
- ✓ physical and chemical properties in the sample components,
- ✓ time of analysis,
- ✓ cost of the measurement apparatus,
- ✓ cost of individual analyses,
- ✓ in the case of the determination of total selenium content or its specific compounds in a given sample, it is important that the applied technique allows for the sample to be brought to such a form where this determination is possible.

Figure 5 presents schematic information on analytical procedures which can be used to determine selenium and its compounds. These methods usually consist of a separation technique and a measurement system (detector).

Selenium content is determined in environmental samples from different origins. Table 4 presents examples found in literature of analytical techniques used to determine total selenium content, or to determine its individual compounds (selenium speciation).

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From the presented literary information, it appears as though determination of total selenium content in a given sample is usually preceded by mineralization assisted by microwave radiation, while determination is performed with AAS using different types of atomization or by ICP-MS. However, in order to conduct selenium speciation for the isolation of individual compounds from a sample, different extraction techniques are used, most often water or enzymatic extraction. The determination of the content of individual compounds is mainly conducted based on coupling chromatography (especially HPLC) with inductively coupled plasma spectrometry (ICP-MS). This analytical procedure has some advantages. Separation can be done in different modes (reverse phase, ion-exchange or size exclusion), so the non-volatile compounds of high and low molecules weight can be directly determine by this versatility procedure. However, also GC is used for selenium speciation, mainly for determine volatile selenium species like CH₃SeH, (CH₃)₂Se and/or (CH₃)₃Se⁺. GC can be also applied to non-volatile Se species after derivatization (with e.g. ethylchloroformate, isopropylchloroformate, diethyl ethoxymethylenemalonate), but this method is time-consuming.

In summary, determination of selenium compounds is now very common area in analytical chemistry, because of selenium importance for human growth and health. For now techniques based on coupling chromatography (especially HPLC) with inductively coupled plasma spectrometry (ICP-MS) are consider to be the most feasible and potential analytical tools for selenium speciation. Although there are a lot of publications about different selenium compounds determination, the accuracy of determination is rarely demonstrated there. This is because of lack of (certified) reference materials for selenium speciation and therefore validation of selenium speciation is not easy task.

Selenium speciation is not easy task, because:

- ✓ Se is present in environmental samples at very low concentrations and in many different forms,
- ✓ of the lack of (certified) reference materials for selenium speciation and thus problem with validation.

However, the number of selenium species, detected by chromatographic separations coupled with inductively coupled plasma mass spectrometry, is growing. There are also new hyphenated techniques, which can be used to determine some specific selenium compounds.

Therefore further studies about determination of selenium compounds and/or discovering of new important selenium compounds are necessary to better understanding of selenium importance for life.

7. Summary

Ever since the benefits of selenium and its compounds for human health has been known, including its growth, development and protection against various diseases and illnesses, more importance is being given to research regarding its level in humans and the possibility of supplementing its content, for example using different supplementation methods and techniques. The most commonly used supplementation method is fertilization of soils enriched with inorganic forms of selenium or the use of pharmaceutical products containing various forms of selenium (usually SeMet or selenium-enriched yeast). The results of many studies also indicate other health promoting effects of selenium, mainly SeMSeCys – the precursor of methylselenol –

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most likely the compound containing anti-cancerous properties. SeMSeCys mainly appears in selenium-enriched plants from the *Allium* and *Brassica* family.

Due to the various forms of selenium as well as their properties, and also because of the very small difference in Se content, which is an indicator of its deficiency or excess in the body, the following is important:

- ✓ the identification of an effective and rapid method allowing for the determination of a given form of selenium in environmental samples (including food supplements) with high accuracy and precision,
- ✓ the development of a method allowing for the determination of the bioavailability and/or bioaccessibility of a given selenium compound in an analyzed product.

They should also be properly validated, which means that it is important to conduct research on the development of new reference materials for the determination of total selenium (needed when determining selenium in the human body) and for the needs of selenium speciation (in order to improve knowledge on the subject of the content of certain significant, and likely beneficial to humans, selenium compounds).

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TABLES**Table 1:** Literary information regarding daily selenium dose ($\mu\text{g}/\text{day}$) in different countries

COUNTRIES	DAILY Se DOSE ($\mu\text{g}/\text{day}$)	LITERATURE
Saudi Arabia	75-121,65	(Al-Ahmari 2009)
China (Keshan region)	3-11	(Dumont et al. 2006)
China (Suzhou region)	43,9	(Gao et al. 2011)
Croatia	27,3	(Klapec et al. 2004)
Egypt	49	(Hussein and Bruggeman 1999)
Greece	39,3	(Pappa et al. 2006)
Spain	72,6	(Diaz-Alarcon et al. 1996)
Japan	133	(Dumont et al. 2006)
Canada	98-224	(Gissel-Nielsen 1998)
Korea	57,5	(Choi et al. 2009)
Libya	13-44	(El-Ghawi et al. 2005)
Lithuania	100	(Golubkina et al. 1992)
Norway	80	(Meltzer et al. 1992)
Poland	30-40	(Wasowicz et al. 2003)
Slovakia	38,2	(Kadrabova et al. 1997)
United States	60-160	(Longnecker et al. 1991)
Switzerland	70	(Dumont et al. 2006)
Sweden	38	(Dumont et al. 2006)
Turkey	30	(Dumont et al. 2006)
Great Britain	34	(Barclay et al. 1995)

Table 2: List of 10 products containing the largest quantity of selenium (USDA Website)

Ranking	Product	Selenium content ($\mu\text{g}/100 \text{ g}$ product)	Other properties
1	Brazil nut	1917	great source of magnesium
2	Sea food: Pacific oysters Blue mussels Whelk	154 90 90	great source of iron , zinc , copper , and vitamin B₁₂
3	Lamb liver	116	packed with nutrients
4	Fish: Orange roughy Canned: tuna, anchovies, swordfish	88 52	a heart healthy food; a good source of protein ; rich in vitamins B₁ , B₂ , B₃ , B₆ , and B₁₂
5	Sunflower seeds	79	great source of vitamin E , iron , vitamin B₁ (thiamin) , B₆ , protein , magnesium , potassium , and copper
6	Bran: Wheat bran Oat bran Rice bran	78 3 17	
7	Caviar	65,5	a great source of iron , protein , and vitamin B₁₂
8	Bacon Lean pork chops	65 43	high cholesterol food
9	Lobster Crab	59,2 47,6	
10	Shrimp	39,6	high cholesterol food ; rich in iron

Table 3: Advantages and limitations of using selenium-enriched yeast as a dietary supplement
(Rayman 2004)

BENEFITS	LIMITATIONS
Contains mainly SeMet	The possibility of allergies
Can be helpful in countries where a selenium deficiency exists	Se-yeast is likely to be perceived as its variability with respect to its selenium content and speciation
Can optimise plasma glutathione peroxidase activity	SeMet from Se-yeast can build up in body tissues to toxic levels
Se-yeast is the most inexpensive organic Se supplement	It appears to be a less-effective anti-carcinogen, than SeMSeCys (produced by garlic and broccoli) and slightly less effective than selenite
It shows efficacy in human anti-cancer intervention studies	
It is a better precursor for selenoproteins synthesis than SeMSeCys, which is largely converted directly to methylselenol	
Se-yeast is the nearest product to food-form Se that is readily available for fortification or supplementation	

Table 4: Information from the literature on the possibilities of using different analytical procedures for determining selenium and/or its compounds

DETERMINATION TYPE	SAMPLE	SAMPLE PREPARATION and/or SEPARATION TECHNIQUE	MEASURING SYSTEM (DETECTOR)	REFERENCES
total Se	coal, fly ashes, sorbents for flue gas cleaning	microwave digestion	ICP-MS and/or HG-ICP-MS	(Diaz-Somoano et al. 2004)
total Se	blood samples	microwave digestion	GC-MS	(Ducros et al. 2000)
total Se	garlic	wet-digestion with HClO_4 and HNO_3	CSV	(Inam and Somer 1999)
total Se	garlic, onion	preconcentration with DAB (3,3-diaminobenzidine) reagent on the activated carbon	ET-AAS	(Izgi et al. 2006)
total Se	fish, shellfish	microwave-assisted wet digestion	FI-HG-AAS	(Lavilla et al. 2007)
total Se	plant materials	slurry preparation; ultrasonic slurry sampling; electrothermal vaporization	ICP-MS	(Li et al. 1998)
total Se	vegetable and fruit samples	ultrasound assisted-hollow fibre liquid-phase microextraction	GF-AAS	(Shrivyas and Patel 2011)
total Se	beer	preconcentration	ICP/MIP-OES	(Tyburska et al.

		using baker's yeast; hydride generation and SPME		2011)
total Se	tea leaves	wet digestion	HG-AFS	(Zhang et al. 2011)
total Se	B.juncea, yeast	microwave digestion	ICP-MS or ET-AAS	(Khakachchi et al. 2004)
total Se	sediment samples	aqua regia digestion	GF-AAS or ICP-MS	(Ochsenkuhn-Petropoulou et al. 2003)
total Se	water	dispersive liquid liquid microextraction	GF-AAS	(Bidari et al. 2007)
total Se	Se-enriched flour and Se-enriched bread	microwave assisted digestion	ICP-MS	(Hart et al. 2011)
total Se	plant material	acid digestion	ICP-AES	(Prins et al. 2011)
total Se	yeast	separation of the cells on nitrocellulose Synpor filters; washed; freeze-dried	INAA	(B'Hymer and Caruso 2006)
Se oxidation states	rock samples	drying, grinding, homogenizing	bulk XAFS spectroscopy	(Ryser et al. 2005)
Se oxidation states	Se-yeast, mineral supplement, sodium selenite, sodium selenate	few milligrams of samples were fixed onto an aluminum sample holder "as-is" using Kapton tape	XANES spectroscopy	(Christensen et al. 2004)
inorganic Se speciation	citric juice	all samples were homogenized; microwave on-line prereduction of Se(VI) to Se(IV)	FI-HG-AAS	(Buguera et al. 1996)
inorganic Se speciation	orange juice	all samples were homogenized; microwave on-line prereduction of	FI-HG-AAS	(Gallignani et al. 2000)

		Se(VI) to Se(IV)		
inorganic Se speciation	sediment samples	phosphoric acid extraction	HPLC-ICP-MS	(Orero Iserte et al. 2004)
inorganic Se speciation	potatoes	homogenization, enzymatic hydrolysis; microwave digestion	DPCSV	(Ferri et al. 2007)
Se speciation	animal tissues (tuna and mussels samples)	enzymatic digestion with non-specific protease	HPLC-ICP-MS	(145 Angels Quijano et al. 2000)
Se speciation	mushroom proteins	extraction with acid, extraction with base, enzymatic extraction	RP-HPLC-ICP-MS	(Gergely et al. 2006b)
Se speciation	human liver tissues, serum, urine	cytosolic extraction	RP-HPLC-ICP-MS	(Hongwei et al. 2006)
Se speciation	<i>B.juncea</i> , yeast	enzymatic hydrolysis, HCl acid extraction	HPLC-ICP-MS	(Khakachchi et al. 2004)
Se speciation	sediment samples	extraction by methanol or HCl	SAX-ICP-MS or RPC-ICP-MS	(Ochsenkuhn-Petropoulou et al. 2003)
Se speciation	soil samples	microwave assisted acid digestion; Extractions by ultrapure water, 0.1 mol L ⁻¹ phosphate buffer ($\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$) at pH 7 and 0.1 mol L ⁻¹ sodium hydroxide	HPLC-ICP-MS	(Tolu et al. 2011)
Se speciation	selenium nutritional supplement	enzymatic extraction	IP-RP-HPLC-ICP-MS	(Zheng et al. 2000)
Se speciation	selenium nutritional supplement	capillary electrophoresis	UV detector	(Sun et al. 2004)

Se speciation	aqueous selenium standards	capillary electrophoresis	ICP-MS	(Bendahl et al. 2001)
Speciation	rice	enzyme assisted extraction; capillary electrophoresis	ICP-MS	(Zhao et al. 2011)
Speciation	yeast-based and yeast-free selenium supplements	enzymatic digestion (for HPLC analysis); headspace extraction and derivatization (for GC analysis)	HPLC-ICP-MS andGC-AED	(Amoako et al. 2009)
Speciation	Se-enriched flour and Se-enriched bread	proteolitic digestion	HPLC-ICP-MS	(Hart et al. 2011)
speciation (hydrophilic Se compounds)	Se-yeast	water extraction and size exclusion chromatography	ICP-MS or ESI Q-TOF MS/MS	(Far et al. 2010)

FIGURES

Figure 1. A diagram of the metabolism process of selenium compounds in humans and animals (Rayman et al. 2008; abdulah et al. 2005; Finley 2005b; Tapiero et al. 2003; Ip 1998; Rayman 2004; Kobayahu et al. 2002; Bendahl and Gammelgaard 2004)

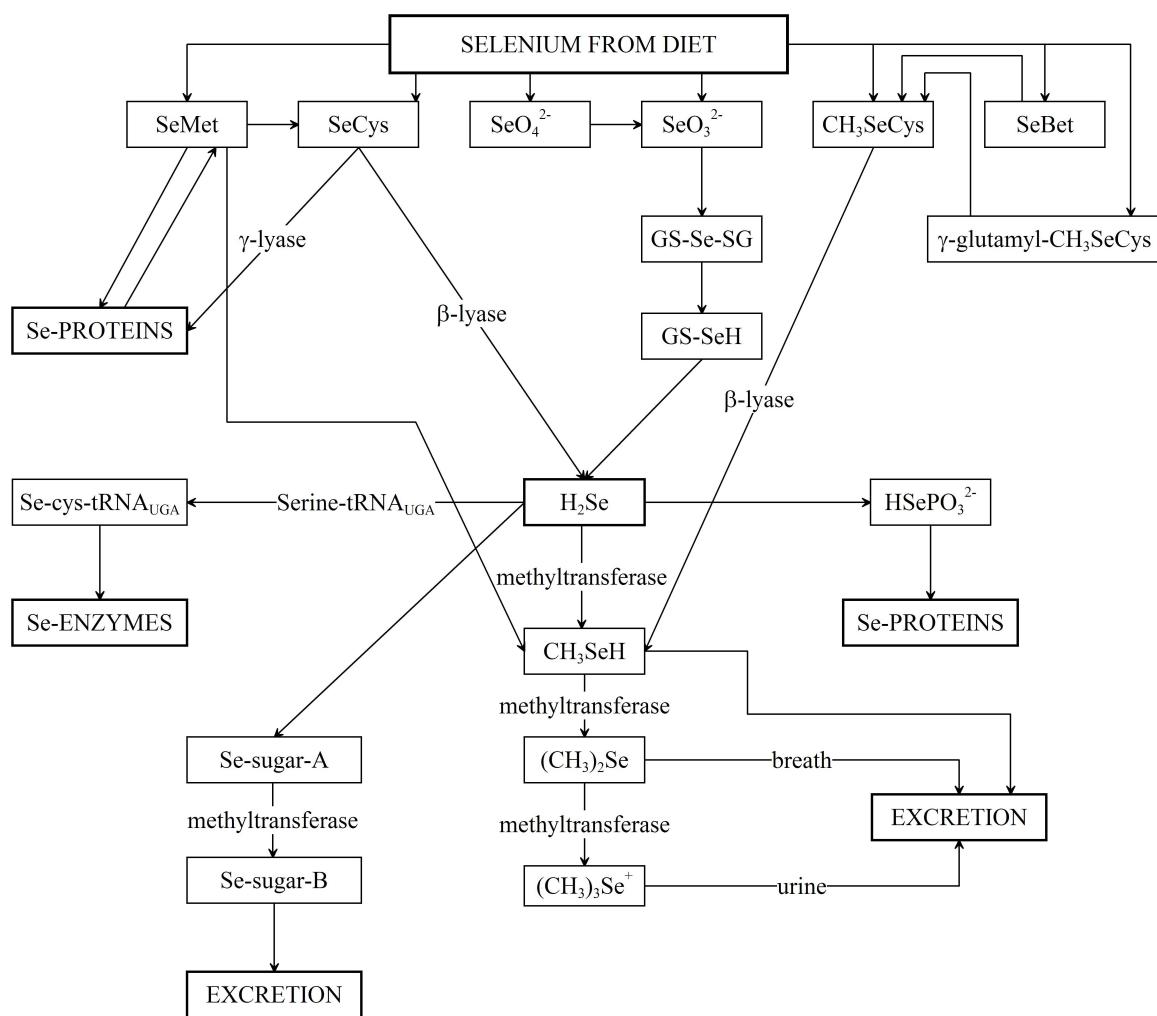


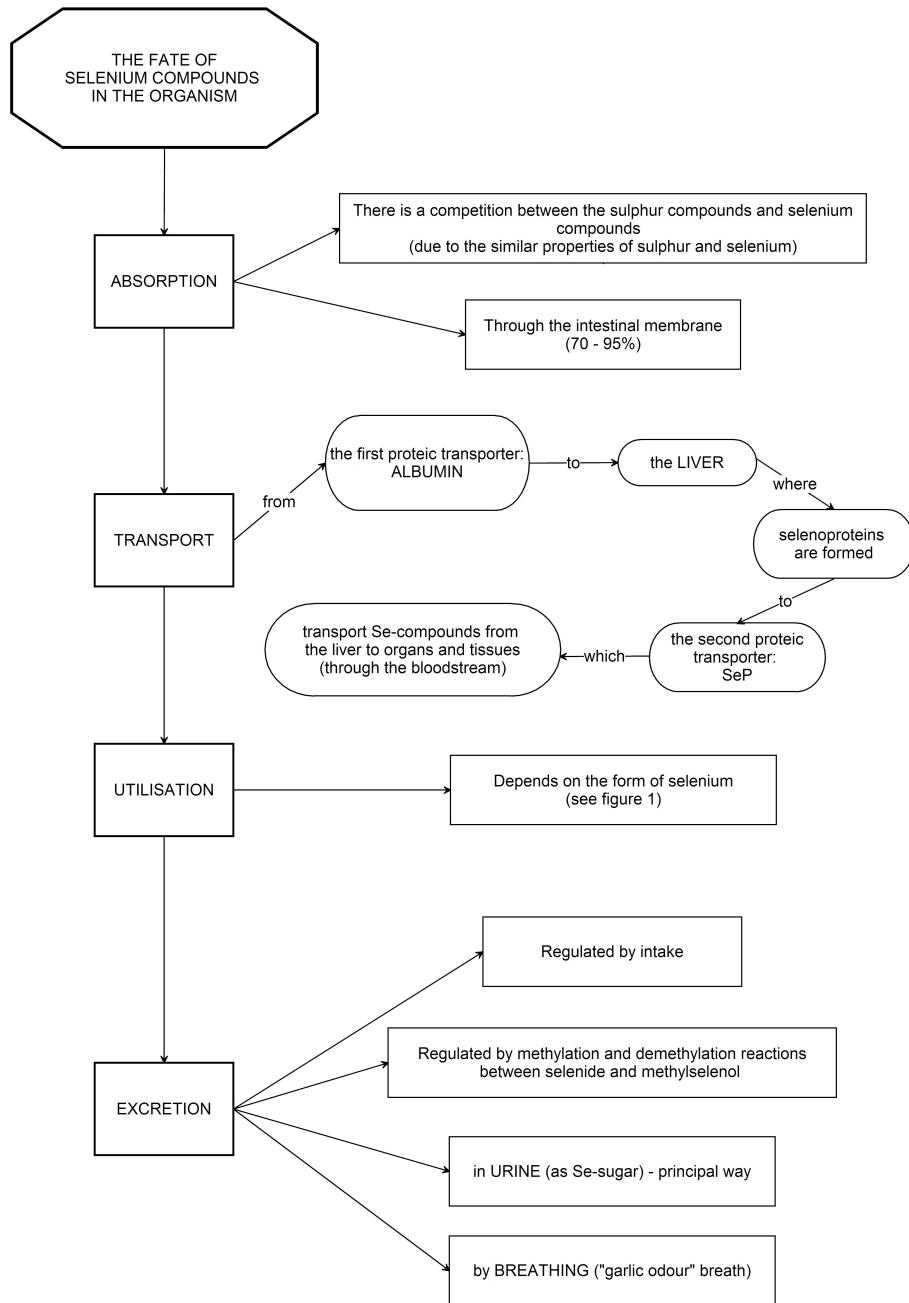
Figure 2. The fate of selenium compounds in the organism (Thiry et al. 2012)

Figure 3. Selenium content in two types of flour and bread [mg/kg dry mass] before and after fertilizer supplementation in Finland (Eurola et al. 1990)

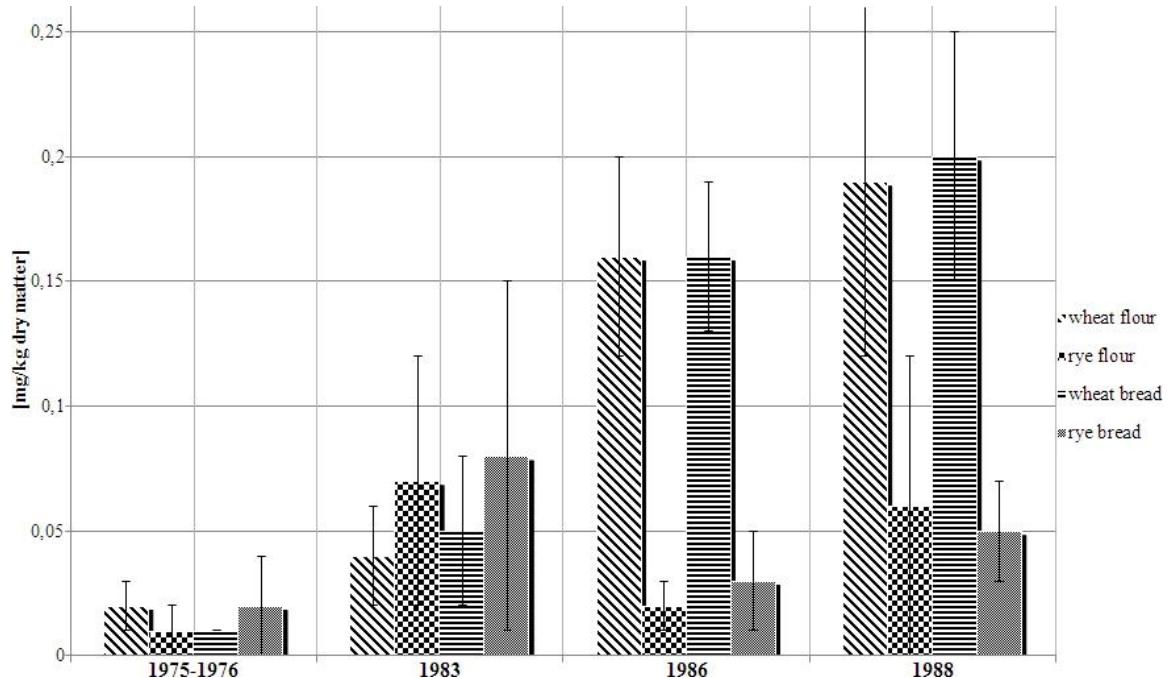


Figure 4. SeMet content in selenium enriched yeast from different manufacturers (%) (Rayman 2004)

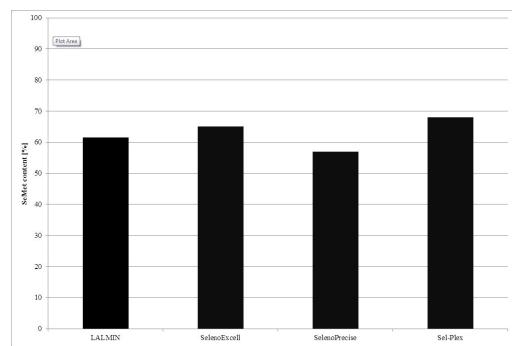


Figure 5. Analytical procedures for determining selenium and its compounds (Pyrzynska 2009; Pyrzynska 2001; B'Hymer and Caruso 2006; Czauderna et al. 1996; Wojciechowski and Bulska 2007; Wysocka and bulska 2007; Wake et al. 2004)

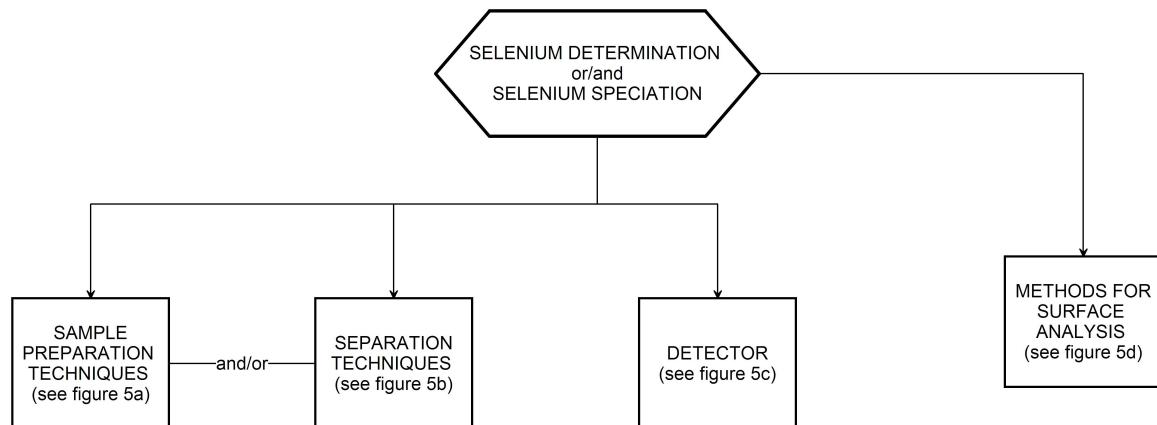


Figure 5a. Schematic information on sample preparation techniques

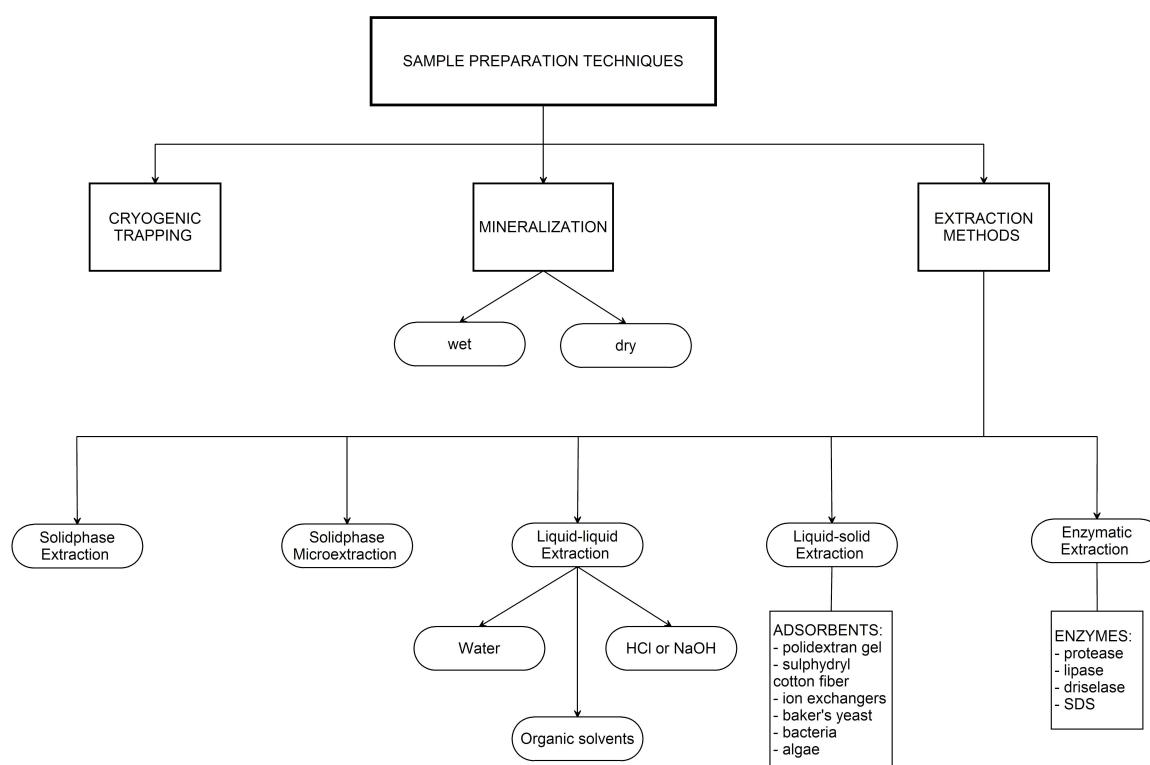


Figure 5b. Schematic information on separation techniques

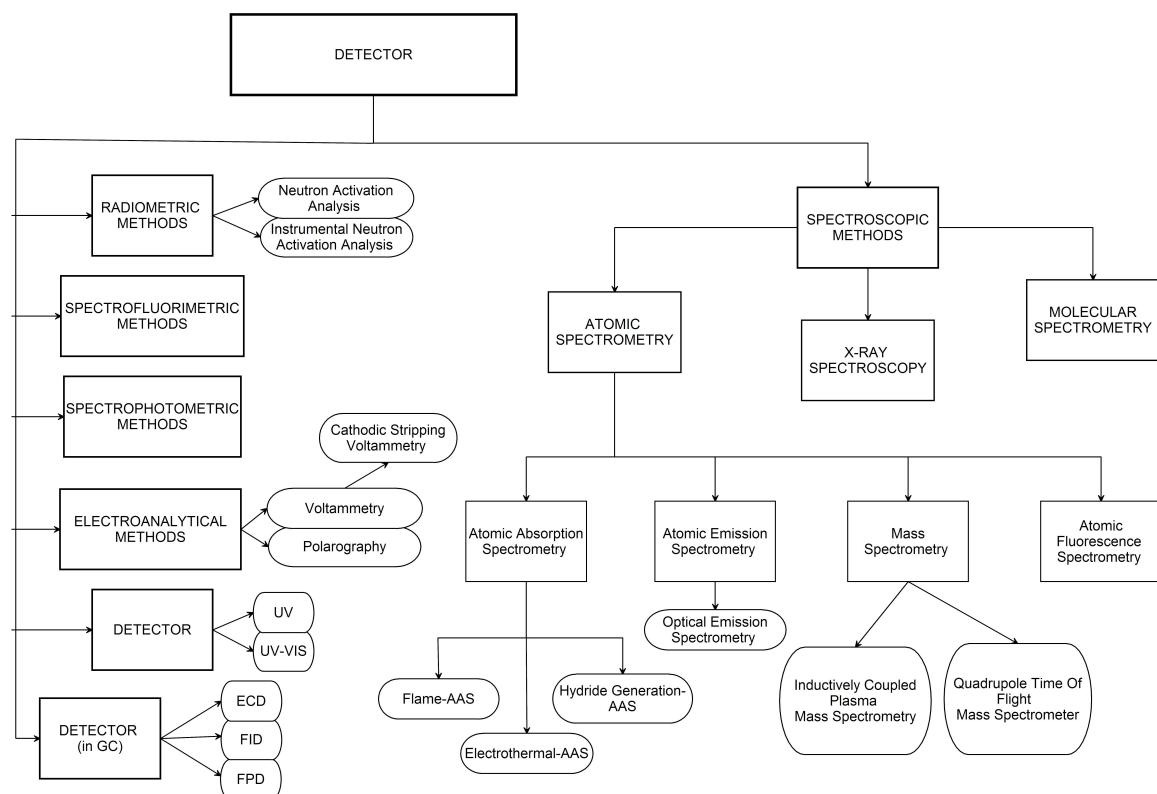
Figure 5c. Schematic information on detection systems

Figure 5d. Schematic information on methods for surface analysis

