Journal of Food Composition and Analysis 71 (2018) 28–35

Contents lists available at ScienceDirect

Journal of Food Composition and Analysis

journal homepage: www.elsevier.com/locate/jfca

Original research article

Selenium speciation in chicken breast samples from inorganic and organic selenium fed chickens using high performance liquid chromatography-inductively coupled plasma-mass spectrometry

Sezgin Bakırdere[a,*], Mürvet Volkan[b], O. Yavuz Ataman[b]

[a] Department of Chemistry, Yıldız Technical University, 34210, İstanbul, Turkey
[b] Department of Chemistry, Middle East Technical University, 06800, Ankara, Turkey

ARTICLE INFO

Keywords:
Food analysis
Selenium
Speciation
HPLC-ICP-MS
Chicken
Food composition

ABSTRACT

Speciation of selenium in chicken breast samples was performed by anion and cation exchange HPLC systems combined with ICP-MS. Samples were categorized into three groups consisting of Control Group, Inorganic Se Fed Group and Organic Se Fed Group. After the optimization of speciation parameters, selenomethionine, selenocystine, Se(IV) and Se(VI) were determined in the samples using the HPLC-ICP-MS system. Instrumental limit of detection values for selenium(IV), selenium(VI), Se in selenomethionine and Se in selenocystine were found to be 0.75, 0.80, 0.55 and 0.46 ng mL^{-1}, respectively. Protease XIV enzyme in 30.0 mM Tris HCl buffered to pH 7.2 was used in the extraction of selenium species from the sample matrix. Total selenium concentrations in the Control, Inorganic Se Fed and Organic Se Fed groups were found to be 675 ± 85, 1084 ± 198 and 887 ± 139 ng g^{-1} based on dry mass, respectively. The concentration of selenomethionine in the Organic Se Fed Group was found to be higher than those in the Control and Inorganic Se Fed Groups. Se(IV) was determined only in the Inorganic Se Fed Group.

1. Introduction

Selenium is known as a crucial element and an essential nutrient for human health. Toxicity and bioavailability of selenium depend on both its chemical form and concentration (Besser et al., 1993). The function of each selenium species in the human body is different. Important roles of this element in different enzymes such as glutathione peroxidase, iodothyronine deiodinase and thioredoxin reductase have been proved in literature (Rayman, 2000). It has been reported that health problems such as nausea, vomiting, and diarrhea may occur in the case of short-term oral exposure to high amounts of selenium. Hair losses, nail brittleness, and neurological abnormalities occur when the exposure dose of selenium is very high (selenosis) (Selenium, 2003). The antioxidant function of selenium in protecting the human body from oxidative effects of oxidants such as hydrogen peroxide, lipid hydroperoxides and their derivatives has been reported in literature (Li et al., 2007). In addition, the preventive role of this element from acne, multiple sclerosis, ovarian cysts, cervical dysplasia, Parkinson disease, colorectal cancer, psoriasis, esophageal cancer, and stomach cancer have been reported (Selenium, Nutrition and Health, 2005). Bioavailability of selenium in yeast-based intervention agents used in cancer chemoprevention studies has also been presented in literature (Larsen et al., 2004). Selenium is crucial at the level of 0.10–0.20 mg/kg in animal diets, and its recommended daily allowance (RDA) has been reported as 55 µg day^{-1} for both men and women (Zeng et al., 2013; Whanger, 2004). The upper tolerable nutrient intake level (UL) for adults is 400 µg day^{-1}. Therefore, the maximum selenium concentration in dry diet should be lower than 2.0 mg kg^{-1}, so as to balance the intake level. Hence, UL of 400 µg day^{-1} of selenium for humans provides an adequate margin of safety (FAO and WHO, 2002). Due to its importance, scientists have performed studies on its bioavailability in different matrices (Moreda-Piñeiro et al., 2017). There are some studies in literature about the bioaccessibility of selenium species in variety of food samples (Khanam and Platel, 2016).

Selenium is also an important element for other living beings including poultry animals. They take in the selenium via feed. In case of deficiency, different diseases such as pancreatic entropy, muscular dystrophy, reduced egg production, increased dead-in-shell chicks, low chick weights at hatching and retained placenta may occur (McCartney, 2006). In general, poultry feed is divided into two groups; a) Natural feedstuffs including corn or soybean meal b) Supplemental sources including sodium selenite. Selenium non-accumulator plants such as corn,

* Corresponding author.
E-mail address: bsezgin@yildiz.edu.tr (S. Bakırdere).

https://doi.org/10.1016/j.jfca.2018.05.005
Received 2 September 2017; Received in revised form 9 May 2018; Accepted 13 May 2018

wheat, or oats are commonly used for animal diets (Payne, 2004). It has been reported that the concentration of selenium that is mainly selenoamino acids, selenomethionine (SeMet) and selenocysteine (SeCys), in natural animal feed ranges between 0.03–0.12 mg kg^{-1} (Kuricova et al., 2003). In order to eliminate any possible health problems caused by selenium deficiency, poultry feed are widely supplemented with various selenium sources. In general, organic and inorganic selenium (selenite or selenate) have been used for supplementation. Although organic selenium supplementation has many advantages, inorganic selenium species such as sodium selenite are still widely used in some countries, (Kuricova et al., 2003). Selenium is transferred into the egg yolk where the embryo is formed and grows. It is reported that supplying selenium via selenium containing yeast causes the enhancement of Se content in the form of SeMet in meat, milk and eggs. Hence, selenium supplementation is mostly done using SeMet (McCartney, 2006). Natural foods containing relatively high selenium content have been recommended as a way of selenium intake. Selenium enriched bread can be used for this aim (Lazo-Velez et al., 2015). Actually, this approach is very useful due to the high consumption rate of bread in many countries including Turkey. In some countries, selenium supplemented products are added to wheat flour to improve the selenium content in bread. For instance, Se-enriched mushroom extract is added to wheat flour in a fortification approach. Actually, it is very difficult to eliminate the global Se deficiency. The poultry industry is another way to minimize this problem, where Se-enriched eggs and meat are being produced for this purpose (Yaroshenko et al., 2004).

There is no doubt that speciation studies provide much more relevant information about the toxicity/bioavailability of elements rather than their total element determination. Hence, scientists have spent tremendous effort to perform accurate determination of analyte species (Güler et al., 2011). In general, different hyphenated techniques based on separation and detection of selenium species with a variety of instruments such as HPLC or GC coupled on-line to a suitable element detector such as ICP-MS have been used in literature for speciation purposes (Bakirdere et al., 2015; Ohta et al., 2009; Oliveira et al., 2016). Speciation studies of selenium in chicken samples are still scarce in literature due to difficulties in the determination. For speciation analysis of selenium, suitable, sensitive and accurate analytical methods are needed. There are few studies in literature that present developed analytical methods for the speciation of selenium in chicken samples (Bierla et al., 2008; Daun et al., 2004).

Selenium speciation study in chicken breast samples from a controlled feeding scenario has not been studied/reported in literature. The main purpose of this study was to perform accurate identification and quantification of selenium species in inorganic and organic selenium fed chicken samples by HPLC-ICP-MS, following an enzymatic extraction under optimum conditions.

2. Materials and methods

2.1. Chemicals and reagents

Chemicals used in this study were of analytical grade/high purity. The stock solution of inorganic selenium species Se(IV) (Aldrich, selenium dioxide, 99.8%, Germany) and Se(VI) (Ventron, sodium selenate, United Kingdom) were prepared in de-ionized water, while organometallic selenium species, seleno-DL-methionine (Sigma, SIS 3875, Germany) and seleno-DL-cystine (Sigma, SIS 1650, Germany) were prepared in 0.10 M HCl. De-ionized pure water (Milli-Q Water Purification System) was used in all sample and standard preparations. Protease XIV (Sigma, SIP 5147, Germany) was the enzyme used to obtain high extraction efficiency. The enzyme was stored at −20 °C. Tris (hydroxymethyl)amino methane hydrochloride (Fluka, FL93363, Switzerland) was used in the extraction step. In the HPLC studies, heptafluorobutyric acid (Aldrich, AL 164194, Germany), trifluoroacetic acid (Fluka, FL 73645, Switzerland), methanol (Merck, Germany), pyridine (Riedel, RH 16037, Germany) and citric acid (Sigma, SIAL 251275, Germany) were used as reagents to prepare mobile phases. DOLT-4 (Dogfish Liver Certified Reference Material for Trace Metals, National Research Council of Canada) was used in the accuracy check of total Se determination. In order to eliminate any possible contamination, all glassware were kept in 2.0 M nitric acid solution when not in use.

2.2. Instrumentation

A Heto FD 8 freeze-drying unit was used to dry samples. Dionex HPLC system equipped with a binary HPLC pump was used to run the mobile phase in gradient elution mode. The HPLC system was connected to an ICP-MS using 85.0 cm tubing having 1.07 mm i.d. and 1.68 mm o.d. This tubing connected the output of the HPLC column to the nebulizer of the ICP-MS. C18 (Dionex C18), C8 (Alltima C8), anion exchange (Spheris S5 SAX), and cation exchange (Spheris S5 SCX) columns were used for the separation of selenium species.

Selenium species were determined using a Thermo X Series ICP-MS system, where there was no reaction/collision. An Ethos Plus Milestone microwave oven was used to digest the chicken samples for the determination of total selenium. A Millipore Stirred ultrafiltration cell (8400 Model) with 10.0 kDa ultrafiltration membrane (Filter Code: YM10 Dia: 63.5 mm, 28.7 cm^2) was used in the filtration of extracted solutions. An Elma, Elmasonic S 40H brand sonication instrument and commercial shaker were used in the extraction studies. A Sigma 2–16 (D-37520 Osterode am Harz, Germany) brand ultracentrifuge instrument was used in the separation of supernatant from residue.

2.3. Procedures

2.3.1. Samples and sample preparation

In the inorganic and organic selenium fed chicken study, chicks were randomly categorized into three groups including Control Group, Inorganic Se Fed Group and Organic Se Fed Group. 225 chicks (Ross 508) were raised in this study. Each group contained 5 sub-experiment groups, with each having 15 chicks. Five chicks were randomly selected from each sub-experiment group and analyzed for their selenium species content. Hence, 75 chicks were analyzed. In the preparation of control group, inorganic and organic selenium fed groups, the same premix and basal diet were used. Hence, determination of selenium in basal diet and premix was not done since a comparison was made using the same background values. For the inorganic selenium fed group, chicks were fed with a diet containing 0.15 mg Se kg^{-1} in the form of Na_2SeO_3. In addition, chicks in the organic selenium fed group were fed with a diet containing 0.15 mg kg^{-1} Se(SeMet) in Sel-plex. For the homogenization of selenium in the diet, selenium species were firstly added to a premix; after homogenization, the premix was mixed with the basal diet to obtain 1000 kg of final diet. Sel-Plex contains organic selenium yeast produced by Saccharomyces cerevisiae CNCM I-3060. Newly hatched chicks were raised for 6 weeks (42 days) in a Vocational School at Balıkesir University, Turkey. Newly hatched chicks were raised in a coop where the temperature, humidity and light were optimum. National Research Council (U.S.) standards were applied throughout the raising process. In the period of 0–3 weeks, a starter diet was used for feeding. At the end of the 3rd week, a grower diet was administered until the end of the 6th week. At the end of the 42nd day, chickens were cut in a clean room, and their breast and buttock parts were taken. Samples were then transported to Middle East Technical University (METU) Chemistry Laboratory in plastic bags, while keeping the temperature at about 0 °C.

For the analytical procedures, all of the optimizations were performed using samples purchased from the cities of Bursa (2 samples) and Kayseri (2 samples) in Turkey. Chickens were cut in Bursa and Kayseri, and breast and buttock parts of chickens were taken and transported to METU Chemistry Laboratory in a cold box kept at about