

SPECIATION ANALYSIS OF INORGANIC FORMS OF SELENIUM IN CONFECTIONERY PRODUCTS

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Abstract

Owing to its biological properties the microelement selenium has attracted enormous interest. It has been established that selenium stimulates the human immune system and has anti-carcinogenic effect. The main sources of selenium are high-protein foodstuffs of plant and animal origin, as well as high-protein dairy products.

The aim of this study was to detect selenium content in confectionery products using speciation analysis in order to determine inorganic forms of selenium such as Se^{2-} , SeO_3^{2-} and SeO_4^{2-} anions.

The hydride generation method combined with the atomic absorption spectroscopy was used for the final determination of selenium forms. The determination of selenium was conducted using aqueous extraction and digestion of samples with concentrated acids.

The speciation determination of selenium was conducted in ten confectionery products.

The correlation between the total content of selenium and its individual forms (-II), (IV),(VI) of different oxidation degree was also examined. It was shown that there was no correlation between the total selenium and inorganic forms of selenium. That means that speciation analysis is the only correct analysis of selenium content in foods.

Key words: selenium, analysis, speciation, mineral confectionery products.

ANALIZA SPECJACYJNA NIEORGANICZNYCH FORM SELENU W WYROBACH CUKIERNICZYCH

Abstrakt

Jednym z mikroelementów, który w ostatnich latach wzbudza ogromne zainteresowanie ze względu na swoje biologiczne właściwości, jest selen. Stwierdzono, że w organizmie człowieka selen stymuluje układ immunologiczny oraz działa przeciwnowotworowo. Głów-

nym źródłem selenu jest żywność bogata w białko pochodzenia zwierzęcego i roślinnego oraz wysokobiałkowe produkty mleczne.

Celem pracy było poznanie specjacji selenu w próbkach wyrobów cukierniczych zmierzającej do określenia nieorganicznych form selenu w postaci anionów: selenkowych Se^{2-} , selenianowych (IV) SeO_3^{2-} , selenianowych (VI) SeO_4^{2-} .

Do oznaczeń końcowych zastosowano technikę generowania wodorków w połączeniu z metodą atomowej spektroskopii absorpcyjnej HG-AAS. Oznaczenie selenu opiera się na połączeniu ekstrakcji wodnej próbki z roztwarzaniem próbki stężonymi kwasami.

Oznaczenie specjacyjne selenu wykonano w 10 próbkach wyrobów cukierniczych.

Zbadano również korelację między zawartością selenu a poszczególnymi formami selenu na (-II), (IV),(VI) stopniu utlenienia. Wykazano brak korelacji między zawartością całkowitą selenu a nieorganicznymi formami selenu. Oznacza to, że analiza specjacyjna jest jedyną analizą zawartości selenu w żywności.

Słowa kluczowe: selen, analiza, specjacja, wyroby cukiernicze.

INTRODUCTION

Investigations on speciation of selenium most often concern samples of physiological liquids such as urine, blood and serum (PYRZYŃSKA 1998). At present speciation of this element is also examined in soils and in plants.

Speciation analysis of selenium deals mainly with two groups of relationships: volatile alkyl derivatives of selenium $(\text{CH}_3)_2\text{Se}$ and $(\text{CH}_3)_2\text{Se}^2$ and non-volatile selenium compounds including inorganic selenium oxoanions Se(IV) and Se(VI), as well as selenoamino acids, e.g. selenomethionine or selenocysteine (PYRZYŃSKA 1998, 2000). Volatile organic compounds of selenium are usually separated from the main components of a sample concentration on a solid sorbent such as glass wool or active carbon, packed in chromatographic columns or compressed in dishes with liquid nitrogen, a then thermally desorbed or extracted with organic solvents. PYRZYŃSKA (2000) established that speciation analysis of non-volatile compounds of selenium occurring in natural waters involved determination of the content of selenium in three samples following their appropriate preparation: 1. In a primary sample the content of Se(IV) is determined with oxidation methods suitable for this stage of analysis. 2. Following the mineralization of samples and oxidation of Se to organic forms (IV), the sum of Se(IV) + Se(-II) was determined. 3. In the mineralised sample Se(VI) was reduced to Se(IV) with an aid of hot concentrated HCl to determine the content of total selenium [the sum Se(IV) + Se(VI) + Se(-II)]. Concentrations Se(VI) and Se(-II) are defined by a difference between individual signs. High performance liquid chromatography (HPLC) is used in investigations of speciation of selenium. Other universally applied methods of detection, e.g. UV-VIS spectrophotometry or conductometry cannot be applied because of interference caused by typically large quantities of nitrates, sulphates or the phosphates as well as

many organic compounds. The recommended determination systems join separation techniques with detection methods specific for selenium, e.g. GF-AAS, ICP-AES, ICP-MS. Unlike wide-range investigations on total content of selenium, little information has been published on inorganic speciation and organic form of this chemical element. Studies on speciation of selenium in Poland have up to now been very scarce. The articles by ŚWIETLIK (1998), HULANICKI (1997) and PYRZYŃSKA (1995, 1998, 1999, 2000) contain mainly theoretical considerations. DEJNEKA'S work (2000) is exceptional in that the author carried out speciation of selenium in cereals, herbs and nutrients for babies, which revealed insignificant content of Se(IV) and Se(VI) in the above products. Thus, it seems advisable to carry out more studies involving speciation analyses of selenium, an essential trace element, in organic samples, including foodstuffs.

The aim of this study was to run speciation analyses of selenium in confectionery products in order to determine inorganic forms of selenium such as Se^{2-} , SeO_3^{2-} and SeO_4^{2-} anions.

MATERIAL AND METHODS

The technique of generating hydrides (HG-AAS) combined with the HG-AAS method can be applied for final determination of selenium in biological samples, e.g. foodstuffs or sewage (BENEMARIYA et al. 1993, CSER et al. 1996, DIAZ et al. 1996, 1997, GILECKI 1997, ASTRUC 1998, GAWŁOSKA and MASŁOWSKA 2000) as it enables researchers to eliminate the influence of the matrix as well as to obtain samples rich in the analyte.

The speciation analysis of selenium in samples of confectionery products, presented in this paper, was based on determination the content of selenium in three samples. The Se determination was preceded by an appropriate preparation of the samples including the following stages:

- in a primary sample selenium (IV), i.e. SeO_3^{2-} , was determined by separating it from the mixture via aqueous extraction in a Soxhlet apparatus;
- the primary sample was mineralised using concentrated nitric acid and Se was oxidised to organic forms (IV) in order to determine Se(IV) + Se(-II), i.e. the sum $\text{SeO}_3^{2-} + \text{Se}^{2-}$;
- the sample was treated with hydrochloric acid (10% solution) in order to reduce SeO_4^{2-} to SeO_3^{2-} and to determine the total content of selenium as well as ($\text{SeO}_4^{2-} + \text{SeO}_3^{2-} + \text{Se}^{2-}$);
- the content SeO_4^{2-} and Se^{2-} was established from the differences between the results obtained at the above determination stages.

The hydride generation method combined with the atomic absorption spectroscopy was used for the final determination of selenium forms. The determination were performed in 6 replications ($n=6$).

The limit of detection was at $0.01 \mu\text{g kg}^{-1}$. The analyte was checked with the use of the certified reference material CRM 402, which showed the total content selenium of $6.70 \pm 0.25 \text{ mg kg}^{-1}$. The total content of selenium in the mineralised reference material subjected to reduction with hydrochloric acid was $5.50 \pm 0.15 \text{ mg kg}^{-1}$, which was lower than the total selenium content in reference material determined by DEJNEKA (2002).

RESULTS AND DISCUSION

The results of determinations of three different forms of selenium as well as total selenium concentration in several confectionary products can be found in Table 1.

Table 1

Results of determination of three of different forms of selenium and total selenium content in samples of confectionery products; $n=6$

Sample of product	Selenium content ($\mu\text{g kg}^{-1}$)			
	$\text{Se}^{2-} \pm \text{SD}$	$\text{SeO}_3^{2-} \pm \text{SD}$	$\text{SeO}_4^{2-} \pm \text{SD}$	Se total $\pm \text{SD}$
Tiki-Tak chocolates	0.09 ± 0.02	1.35 ± 0.42	1.20 ± 0.22	2.65 ± 0.59
Malaga chocolates	0.05 ± 0.01	2.05 ± 0.24	1.42 ± 0.38	3.53 ± 0.46
Kasztanki chocolates	0.04 ± 0.01	1.28 ± 0.31	1.10 ± 0.14	2.42 ± 0.34
Prince-Polo wafers	0.03 ± 0.01	2.30 ± 0.47	1.63 ± 0.87	4.00 ± 0.55
Sesame biscuits	0.06 ± 0.01	2.50 ± 0.35	1.91 ± 0.53	4.43 ± 0.38
Salted breadsticks	0.03 ± 0.01	1.94 ± 0.93	1.83 ± 0.75	3.82 ± 0.74
Delicje biscuits	0.04 ± 0.01	2.43 ± 0.40	1.35 ± 0.32	3.83 ± 0.89
Alibi chocolate bar	0.07 ± 0.01	1.88 ± 0.95	1.50 ± 0.54	3.47 ± 0.55
Amaranth bar	0.03 ± 0.02	1.38 ± 0.47	1.30 ± 0.23	2.71 ± 0.63
Likwor rumowy chocolates	0.08 ± 0.02	1.22 ± 0.33	1.10 ± 0.15	2.41 ± 0.46

SD – standard deviation

The highest total selenium content was found in sesame biscuits ($4.43 \pm 0.38 \mu\text{g kg}^{-1}$), which can be attributed to high selenium content in areas where sesame seeds are harvested. The data in Table 1 show that the remaining confectionery products are characterised by lower SeO_3^{2-} content, within the in range of 1.22 ± 0.33 to $2.50 \pm 0.35 \mu\text{g kg}^{-1}$. Comparatively rich in selenium were Prince-Polo wafers, salted breadsticks and Delicje biscuits. In general, the analysed sweets and biscuits were low in Se^{2-} (0.03 to $0.09 \mu\text{g kg}^{-1}$), SeO_3^{2-} (1.22 ± 0.33 to 2.43 ± 0.40) and especially SeO_4^{2-} (1.10 – $1.91 \mu\text{g kg}^{-1}$). The highest SeO_4^{2-} content was determined in sesame biscuits ($1.91 \mu\text{g kg}^{-1}$). Tiki-Tak chocolates possess the highest content of Se^{2-} ions ($0.09 \mu\text{g kg}^{-1}$). The highest content of SeO_3^{2-} was found in Delicje biscuits ($2.43 \mu\text{g kg}^{-1}$).

The results on determination of selenium ions in confectionary products obtained in the course of the present work cannot be compared to other data as the available references do not contain comparable works.

The correlation between the total content of selenium and its individual forms (-II), (IV),(VI) of different oxidation was also examined. However, no correlation between the total selenium and inorganic forms of selenium was established, which implies that speciation analysis is the only correct method for determination of selenium content in foods. This conclusion is in agreement with the opinion expressed by DEJNEKA (2002).

The experimental investigations proved that with the HG-AAS method it is possible to divide the mixture into three ion forms and simultaneously determined Se^{2-} , SeO_3^{2-} and SeO_4^{2-} in samples of confectionery products. The determination results suggest the content of selenium in confectionery products is low and it does not cover selenium daily demand. Therefore, it seems recommendable to enrich diet with selenium-high products or use dietary supplements, such as selenium yeast or pharmaceuticals including selenium preparations.

CONCLUSIONS

1. The confectionery products examined differ in proportions of selenium ion forms: Se^{2-} , SeO_3^{2-} and SeO_4^{2-} .
2. It was proven that there was no correlation between the total selenium and inorganic forms of selenium. That means that speciation analysis is the only correct analysis of selenium content in foods.
3. In the analysed food products selenium occurred as SeO_3^{2-} (22%), SeO_4^{2-} (12%) and Se^{2-} (only 2%).

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