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## THE DETERMINATION OF CONTENT OF SELENIUM IN NATURAL FRUIT JUICES BY SPECTRAL METHODS

### OZNACZANIE ZAWARTOŚCI SELENU W NATURALNYCH SOKACH OWOCOWYCH METODAMI SPEKTRALNYMI

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*The results of determination of trace quantities of selenium in various commercial natural fruit juices by three independent methods: atomic absorption spectrometry (AAS), spectrophotometry (UV-VIS) and spectrofluorometry (SF) were presented. The level of selenium in any of the analysed samples of fruit juices did not exceed the WHO recommended level of 0.010 mg/l for drinking water.*

**Key words:** selenium, atomic absorption spectrometry, spectrophotometry, spectrofluorometry, determination, natural fruit juices.

**Słowa kluczowe:** selen, absorpcyjna spektrometria atomowa, spektrofotometria, spektrofluorometria, oznaczanie, naturalne soki owocowe.

## INTRODUCTION

Regarding the importance and role of selenium in human nutrition and evaluation of ecological risk, knowledge of selenium content of typical food products is important. Most of the methods are based on application of instrumental analysis [22]. Especially useful were fluorometry, X-ray fluorescence spectrometry, atomic absorption spectrometry, taken from polarography [23], voltammetry and neutron activation [27]. There are also methods based on gas, liquid and gas-liquid chromatography [10-11].

Spectrophotometric methods used coloured complexes to determine selenium with aromatic o-diamine, others used creating colour compounds as a result of oxydation of reagents by selenium [2,6,12]. The method, with usage of 3,3'-diaminobenzidine (DAB), can be used to determine in aquatic environment or after extraction of diphenyl-piazoselenium with toluene.

Fluorometric method is based on measurement of intensity of radiation of diphenyl-piazoselenium fluorescence complexes in non-fluorescence organic solvent [1,14]. Selenium has ability to create this type of compounds in reaction with 2,3- diaminonaphtalene (DAN)

or 3,3'-diaminobenzidine (DAB). According to our previous research fluorometric method is suitable to determine selenium in 1ppb quantity [13,15-16,24].

Atomic absorption spectrometry method is suitable to determine selenium content by -2 degree of oxidation occurring in volatile compounds. Sensitivity of the AAS method is 0,1  $\mu\text{g}/\text{dm}^3$  [4].

Methods to determine selenium used nowadays are suitable to determine selenium content from a dozen to about 1 ppb or even hundredth part ppb.

The aim of the work was to examine selenium content in samples of natural fruit juices by using apparatus i.e. spectrofluorometer Fluorescence Spectrophoto, type F-2000, produced by Hitachi (Japan), spectrophotometer UV/VIS HP-8453 by Hewlett Packard (Germany) and atomic adsorption spectrophotometer GBC Avanta ver 1.3.1. of Australian production.

## MATERIAL AND METHODS

This study present the selenium content in samples of fruit juices available in various shops in Łódź. Testing samples were packed in 1.0 or 0.2 liters cartons. Among the examined samples were: Kubuś, Smakuś, Dick Black, Fortuna and Hortex-fruit and multi-fruit. Most of them contained carrot and apple as ingredients. All natural juices were clear, without any preservatives, pasteurized and made of fresh fruit. Their characteristic was high content of vitamins A, C and E. Nutrition value of juices varied from 36 kcal to 58.4kcal/100g. A glass of juices covered total daily requirement of vitamins A and C. All natural fruit juices had quality certificates.

Apparatus, reagents and solutions, mineralization of samples, preparing samples of solution for analysis were published by *Gawłowska, Masłowska* [7, 17].

To mineralise tested samples a modern instrumentation called Maxidigest MX 350, produced by Prolabo (France) was used with nitric acid and hydrogen peroxide.

Selenium was determined in natural fruit juices by means of spectrofluorometric method, spectrophotometric method and AAS method. Absorbancy readings of tested solution were done at wave length of  $\lambda = 196 \text{ nm}$ . All the experiments were carried out in argon atmosphere. As the reagent 3,3'-diaminobenzidine (DAB) was used. Coloured (yellow) piazoselenium was extracted with toluene which was the best one for extraction. Absorbancy readings of the coloured toluene solutions were taken at the wavelength of  $\lambda = 420 \text{ nm}$  (UV-VIS) or 563/420 nm (SF). The determination were performed in 6 replications (n=6).

The analyte was checked with the use of the certified reference material, which showed the total content selenium of  $2.20 \pm 0.25 \mu\text{g}/\text{l}$ . The total content of selenium in the reference material was  $1.00 \pm 0.04 \mu\text{g}/\text{l}$ .

## RESULTS AND DISCUSION

The calibration curves were linear with very good correlation coefficient ( $r > 0.99$ ). Toluene as solvent of piazoselenium was very useful for determination of trace element of selenium content in natural fruit juices. Recovery of selenium was approximately 85.60-94.80% for AAS method, 86.56-98.60% for spectrophotometric method and 87.50-93.85% for spectrofluorometric method. Evaluation of methods shows that all of them are optimal and give reliable results. Test F-*Snedecora* gave results above one for all methods.

In the table I, obtained results of determination of selenium in examined natural fruit juices by using AAS, UV- VIS and SF methods were presented. Average selenium content in

fruit juices was 0,65  $\mu\text{g/l}$ . Maximum selenium content in fruit juices was 0,94  $\mu\text{g/l}$ . Minimal selenium content in fruit juices was 0,46  $\mu\text{g/l}$ . None of the analysed samples contained elevated levels of selenium. The content of selenium in the examined samples decreases in the following order : Hortex – multi fruit vitamin < Hortex – peach vitamin < Hortex – grapefruit < Kubuś – carrot, peach, apple < Hortex – multi fruit < Hortex – carrot < Kubuś – carrot < Smakuś < Fortuna – carrot < Fortuna – carrot, apple, strawberry < Fortuna – carrot, apple, banana < Fortuna – orange < Dick Black – multi – fruit < Dick Black – grape.

Table I. Selenium content of natural fruit juices as determined by three independent spectral methods: atomic absorption spectrometry (AAS), spectrophotometry (UV- VIS), spectrofluorometry (SF),  $d = 1 \text{ cm}$ ,  $n = 6$

No	Name of juice	Selenium content [ $\mu\text{g/l}$ ]		
		S – standard deviation		
		AAS method	UV-VIS method	SF method
1	Kubuś-carrot, peach, apple	0.75 S = 0.00	0.75 S = 0.01	0.75 S = 0.01
2	Kubuś-carrot	0.68 S = 0.00	0.68 S = 0.01	0.68 S = 0.03
3	Smakuś	0.61 S = 0.00	0.61 S = 0.01	0.61 S = 0.05
4	Hortex-multi fruit	0.73 S = 0.01	0.70 S = 0.01	0.70 S = 0.02
5	Hortex-multi fruit vitamin	0.94 S = 0.01	0.94 S = 0.01	0.94 S = 0.03
6	Hortex-carrot	0.70 S = 0.01	0.74 S = 0.01	0.72 S = 0.01
7	Hortex-peach vitamin	0.90 S = 0.01	0.90 S = 0.01	0.90 S = 0.04
8	Hortex- grapefruit	0.76 S = 0.00	0.69 S = 0.00	0.70 S = 0.01
9	Dick Black - grape	0.46 S = 0.01	0.46 S = 0.01	0.46 S = 0.01
10	Dick Black – multi- fruit	0.51 S = 0.01	0.51 S = 0.01	0.51 S = 0.01
11	Fortuna-black-currant	0.62 S = 0.01	0.68 S = 0.00	0.51 S = 0.01
12	Fortuna- orange	0.55 S = 0.01	0.56 S = 0.00	0.55 S = 0.01
13	Fortuna-karotka carrot, apple, banana	0.57 S = 0.01	0.56 S = 0.00	0.50 S = 0.01
14	Fortuna-karotka carrot, apple, strawberry	0.59 S = 0.01	0.57 S = 0.01	0.57 S = 0.01
15	Fortuna-karotka carrot	0.60 S = 0.01	0.65 S = 0.00	0.69 S = 0.02
16	Fortuna - aronia	0.59 S = 0.01	0.48 S = 0.00	0.54 S = 0.05

The similar selenium content was obtained by three separate methods: AAS, spectrofluorometric and spectrophotometric in natural fruit juices : Kubaś, Smakuś, Hortex (multi-fruit-vitamin, peach-vitamin,) and Dick Black (multi-fruit and grape). The similar selenium content was also determined by AAS and SF methods in orange juice produced by Fortuna. Additionally, identical selenium content was determined by two separate methods: spectrofluorometric and spectrophotometric in fruit juices: by Hortex (multi-fruit), by Fortuna (carrot, apple, strawberry). Only in the case of carrot juice by Hortex selenium content determined by three methods differs slightly in the second figure after the point (0.02%).

Results presented in table I show that the highest level of selenium is included in natural multi-fruit juice with vitamins produced by Hortex. The least level of selenium is included in fruit juices by Dick Black. Results obtained in this study prove that the three methods of determining of selenium are reliable, so AAS, spectrofluorometric and spectrophotometric methods can be used to examine natural fruit juices.

Natural fruit juices examined have relatively low selenium content, which was proved by the experiment. The labels of examined fruit juices lack value of selenium content as valuable microelement declared by producer. Results given in this study are in the scope considered as natural content of this element in juices.

The systematic investigations over content of selenium in Poland were not led in fruit juices so far. It was one should from data the comparing received in this study results of content of selenium different authors [3, 7-9, 17-18, 25-26] they are affirm approximate.

In any of the analysed samples of fruit juices the level of selenium did not exceed the WHO [5] recommended level of 0.010 mg/l (10 µg/l) for drinking water [19-21].

## CONCLUSIONS

1. It was experimentally proved that spectrophotometric, spectrofluorometric and AAS methods can be successfully used to determine trace amounts of selenium in natural fruit juices after their full mineralization.
2. In all samples examined determined selenium content is low and does not exceed acceptable level established by WHO for the drinking water.
3. Maximum content of selenium determined by AAS, spectrophotometric and spectrofluorometric methods is 0.94 µg/l. Selenium content in the analysed samples was in the range of 0.46 µg/l – 0.94 µg/l. Average selenium content in natural fruit juices is 0.65 µg/l. This content is very low and below WHO acceptable level for drinking water (0.010 mg/l).
4. All three methods give similar results of determination of selenium in natural fruit juices and all of them are acceptable.
5. The obtained results also show great variability of content of selenium in examined natural fruit juices.

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Summary

The aim of this study was the evaluation of the content of selenium in natural fruit juices. In this study, the author determined trace quantities of selenium in fruit juices by three independent methods: atomic absorption spectrometry (AAS), spectrophotometry (UV-VIS) and spectrofluorometry (SF). None of the analysed samples contained elevated levels of selenium. Selenium content in the analysed samples was in the range of 0.46  $\mu\text{g/l}$  – 0.94  $\mu\text{g/l}$  average 0.65  $\mu\text{g/l}$ . The level of selenium in any of the analysed samples of fruit juices did not exceed the WHO recommended level of 0.010 mg/l for drinking water.

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OZNACZANIE ZAWARTOŚCI SELENU W NATURALNYCH SOKACH OWOCOWYCH METODAMI SPEKTRALNYMI

Streszczenie

W krajowych naturalnych sokach owocowych oznaczono zawartość selenu, wykorzystując trzy niezależne metody spektralne: spektrofлуorymetrię (SF), spektrofotometrię (UV-VIS) i absorpcyjną spektrometrię atomową (ASA). Zawartość selenu w badanych próbkach mieści się w granicach 0,46  $\mu\text{g/l}$  – 0,94  $\mu\text{g/l}$ , średnia 0,65  $\mu\text{g/l}$ . Wykonane badania pozwoliły wykazać, że naturalne soki owocowe charakteryzują się stosunkowo niską zawartością selenu i nie przekraczają dopuszczalnego poziomu określonego przez WHO dla wody do picia na poziomie 0,010 mg/l (10  $\mu\text{g/l}$ ).

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