

## PREPARATION AND CHARACTERIZATION OF SELENIUM NANOPARTICLES

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**Abstract:** Selenium nanoparticles were prepared with reduction method from sodium-selenite. To stabilize the nanoparticles, two different stabilizers were used. The prepared nanoparticles were characterized with transmission electron microscopy (TEM), with the use of the images the diameters of the nanoparticles were measured which were 70.9 nm in average in case of gum arabics as stabilizer, and 21.7 nm with guar gum. To evidence the presence of the stabilizer layers, Fourier transformation infra-red spectroscopy (FTIR) was used. Applying X-ray diffraction (XRD), the states of the nanoparticles were determined. As a mixture of organic and inorganic selenium compounds, these nanoparticles could provide both fast and slow, long-term uptake for edible plants which could make up the missing amount of Se for human body.

**Keywords:** Selenium nanoparticles, TEM, XRD, FTIR

### INTRODUCTION

Selenium is considered to be an important trace element of the human body [1]. The proper level of selenium has many advantageous effects like protection of immune system, thyroid, and homeostasis [2], furthermore keeping up the ideal amount is a good way to prevent serious illnesses like cancer [3] or Alzheimer [4]. The main cause of these illnesses is the oxidative stress (caused by the free radicals like reactive oxygen and nitrogen species) which is usually neutralized by the glutathione peroxidase protein. For this mechanism, selenium is an important component [5]–[10]. The main source of selenium in everyday life is different edible plants which can uptake the different forms of selenium from the soil [11]. According to The American Recommended Dietary Allowance (RDA), the necessary amount is 70 microgram for men and 55 for women per day [12]. However, in many countries (mainly in Europe) the soils are poor in selenium so there is a high chance for the formation of deficit in human

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body. The selenium deficit already affects about 3 billion people worldwide, meanwhile researchers predict further selenium loss from soils due to the climate change which will further increase their number [13].

Due to the chemical similarity of selenium and sulphur, plants take up the selenium via sulphur transporters [14]. Selenite, selenate, and organic selenium are ideal forms of selenium to uptake for plants. However, selenides and elemental selenium ensure a slow, and lasting uptake because microorganisms in soil first have to transform them to other forms which can be taken up [15]. Nano selenium seems to be the least toxic selenium form, furthermore unlike to the common used selenite and selenate, metallic nano selenium does not inhibit the growing process of the plants, instead it can stimulate the root regeneration [16].

In this paper, selenium nanoparticles were prepared both with organic and elemental selenium content which could ensure both fast and lasting selenium uptake. This could be a lasting solution to increase the selenium amount in the soils and make up the missing amount in the human body through edible plants. The nanoparticles were stabilized with two different non-toxic stabilizers.

## 1. MATERIALS AND METHODS

### 1.1. Materials

For the Se nanoparticle preparation cysteine ( $C_3H_7NO_2S$ ) and sodium-selenite ( $Na_2SeO_3$ ) were purchased from *Reanal*. As a solvent, distilled water was used. Two different stabilizers were used during our experiments, guar gum (*Donauchem*) and gum-arabic (*Reanal*).

### 1.2. Characterization methods

Transmission electron microscopy (TEM) was used to characterize the nanoparticles. For the examination a FEI Tecnai G2 20 X-Twin instrument was used with 200 kV voltage. The sample was dropped on copper grid from water/ethanol suspension. Using the images, the size of the particles was measured by image analysing software (ImageJ).

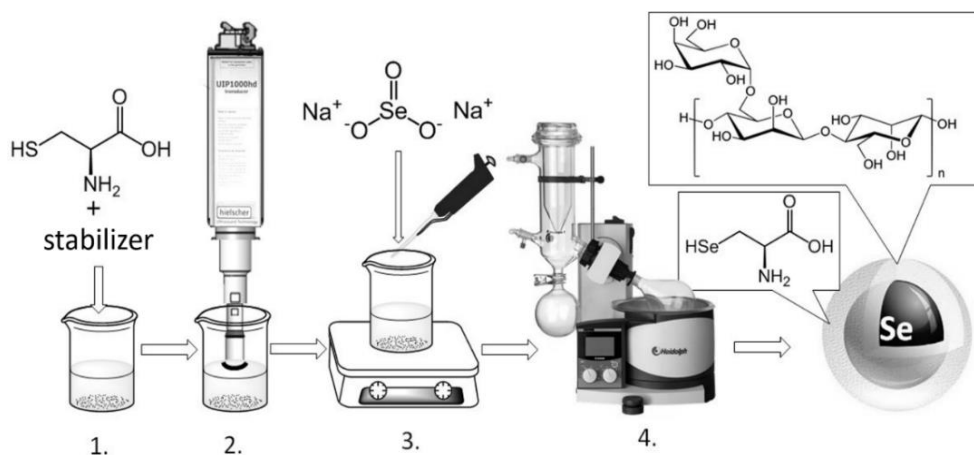
Fourier transformation infra-red spectroscopy (FTIR) was used to evidence the presence of the stabilizers. For the measurement, a Bruker Vertex 70 instrument was used with  $4\text{ cm}^{-1}$  resolution and  $16\text{ s}^{-1}$  scanning velocity.

X-ray diffraction (XRD) was used to detect the different states of Se nanoparticles. For this measurement, a Bruker D8 Advance type instrument was used.

### 1.3. Preparation of stabilized Se nanoparticles

In the first step, 0.4 g cysteine was dissolved in 20 ml distilled water and 5 g stabilizer in 250 ml distilled water (*Figure 1.1*). The two solutions were mixed and homogenized with ultrasonic homogeniser (340 W, 19.42 kHz) for 10 minutes (*Figure 1.2*). For the next step, 0.11 g sodium-selenite was dissolved in 10 ml distilled water and added to the solution in drops during continuous mixing (*Figure 1.3*). After mixing, the

solvent was removed by vacuum-evaporation on 60 °C then the sample was dried on 80 °C overnight (*Figure 1.4*). As a result, stabilized Se nanoparticles were prepared.



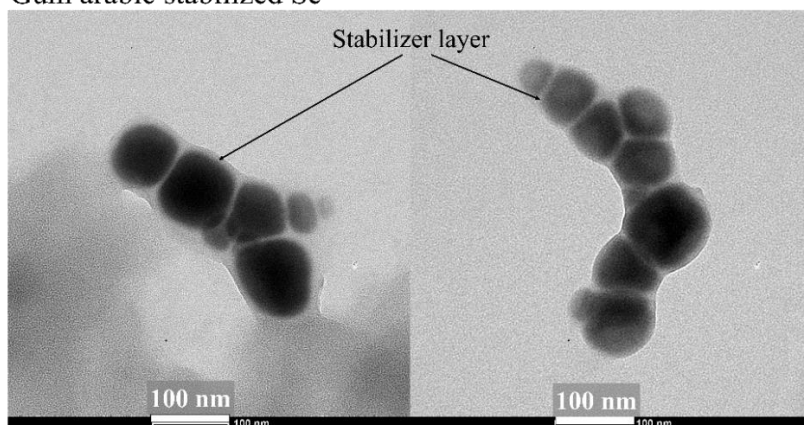
**Figure 1**  
*Preparation process of stabilized Se nanoparticles*

## 2. RESULTS AND DISCUSSION

### 2.1. TEM examinations

TEM was used to characterize the Se nanoparticles shape and size. The gum arabic stabilized nanoparticles had spherical shape (*Figure 2*). The particles were between 20–80 nm diameter with an average of 70.9 nm diameter. The stabilizer layer can be seen around the particles.

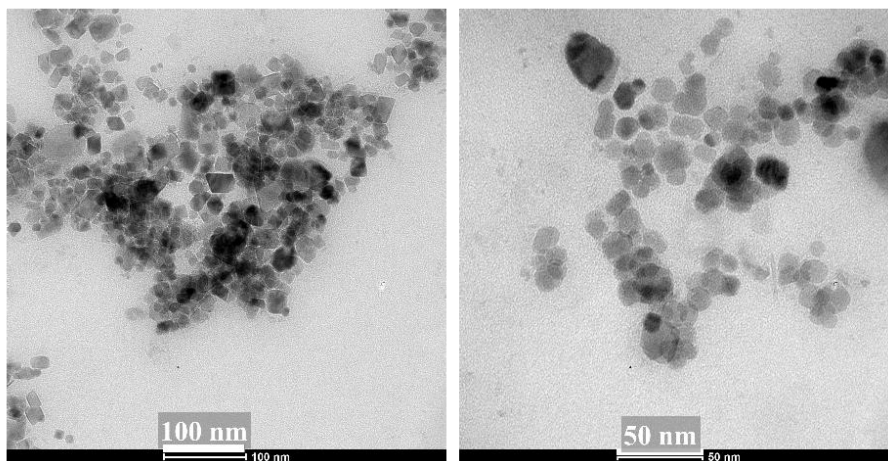
Gum arabic stabilized Se



**Figure 2**  
*SEM image of stabilized Se nanoparticles with gum arabic*

The guar gum stabilized nanoparticles did not have a well-defined shape but they had a significantly lower diameter (average of 21.7 nm) (Figure 3). The vast majority of the particles (80%) were under 24 nm, some particles were bigger with a maximum of 55 nm.

#### Guar gum stabilized Se

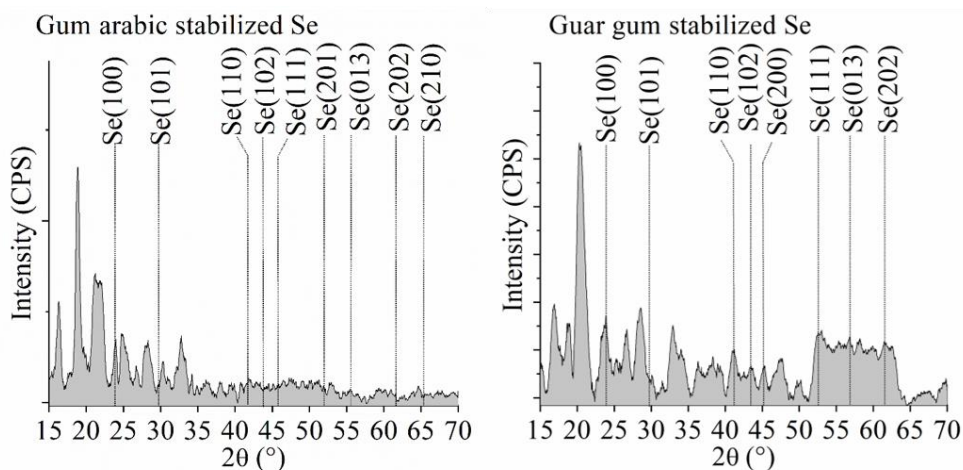


**Figure 3**

*SEM image of stabilized Se nanoparticles with guar gum*

## 2.2. XRD measurements

XRD measurements were used to evidence the success of elemental Se preparation (Figure 4).



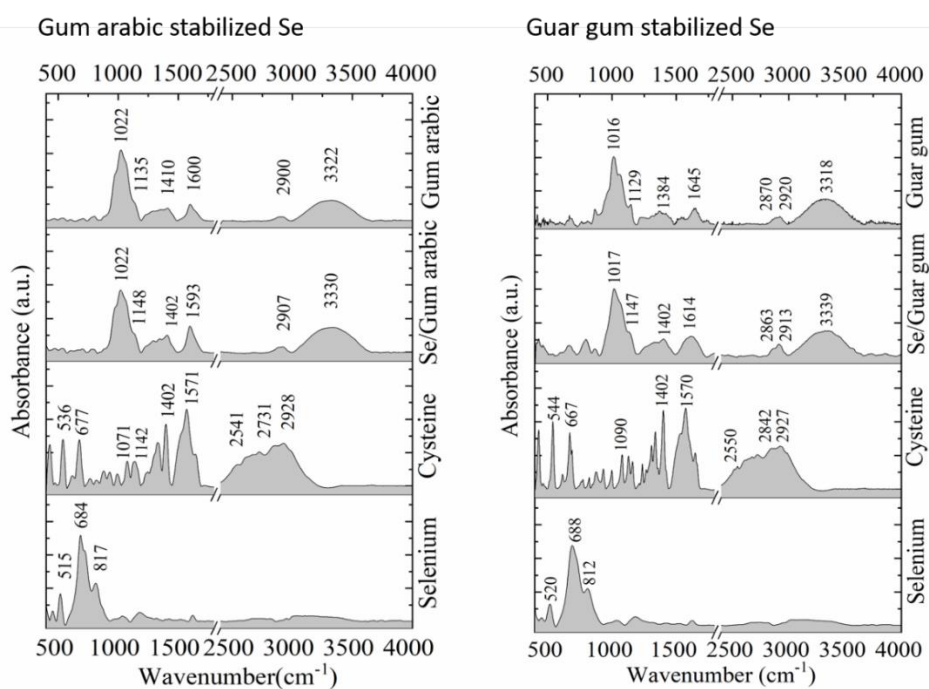
**Figure 4**

*XRD measurements of Se nanoparticles with gum arabic and guar gum stabilizers*

Selenium have many crystal planes which appear on the XRD images: (100) at 23.9°, (101) at 29.8°, (110) at 41.7°, (102) at 43.7°, (111) at 45.8°, (201) at 51.9°, (013) at 55.6°, (202) at 61.5°, and (210) at 65.3° 2 $\theta$  degrees. The presence of crystal planes evidences the metallic form of selenium so the success of the reduction. The crystal planes appeared in case of all the samples.

### 2.3. FTIR measurements

FTIR measurements were used to evidence the presence of the stabilizers on the samples (Figure 5). Comparing the spectrum of the Se containing sample with the spectrum of the components, small shifts have been detected caused by the interactions between the Se and the stabilizer or the cysteine.



**Figure 5**

*FTIR measurements of Se nanoparticles with gum arabic and guar gum*

On the FTIR spectrum of gum arabic stabilized Se nanoparticles the peak of C-O-C bonds was detected at 1,022 cm<sup>-1</sup> in case of both the gum arabic and the selenium contained sample. The  $\nu$ C-O(H) bond appears at 1,135 cm<sup>-1</sup> in the stabilizer, but in case of the sample it shows a small shift (1,148 cm<sup>-1</sup>). The peak of  $\beta$ OH shifts from 1,410 cm<sup>-1</sup> to 1,402 cm<sup>-1</sup>, meanwhile the  $\nu$ OH shifts from 3,326 cm<sup>-1</sup> to 3,332 cm<sup>-1</sup>. These shifts show strong interactions between the Se nanoparticles and the polymer which help the nanoparticle stabilization. The specific peaks of the reducing agent

(cysteine) are not detectable on the spectrum of the sample due to the low quantity. The peaks of selenium are also not visible in the sample because the nanoparticles are coated with the stabilizer.

In case of the guar gum stabilized sample the C-O-C bond appears at 1,016–1,017  $\text{cm}^{-1}$ , while the  $\nu\text{C-O}$  bond of alcoholic and glycosidic hydroxyl groups shift from 1,129  $\text{cm}^{-1}$  to 1,147  $\text{cm}^{-1}$ . The absorbance of  $\beta\text{OH}$  groups shifted from 1,384  $\text{cm}^{-1}$  to 1,402  $\text{cm}^{-1}$ . This shift also means the interact between the Se particles and the stabilizer, and the selenium-cysteine complex formation. The  $\nu\text{OH}$  groups appeared at 3,318  $\text{cm}^{-1}$  in case of the guar gum, meanwhile in thee selenium contained sample it shifted to 3,339  $\text{cm}^{-1}$ . The specific peaks of cysteine and selenium are not visible due to the low quantity.

## CONCLUSION

In this paper selenium nanoparticles were prepared with two different non-toxic stabilizers in order to prepare a Se source which ensures both fast and lasting uptake for plants. For this purpose, selenium contained samples were prepared with both elemental and organic content. The nanoparticles were examined by transmission electron microscopy to characterize their shape and size. The gum arabic stabilized sample had an average 70.9 nm diameter and well-defined spherical-like shape, meanwhile the guar gum stabilized sample had an average of 21.7 nm diameter with irregular shape. X-ray diffraction was used to evidence the success of the reduction step and to determine the crystal planes of Se. The measurement showed the presence of elemental (metallic) Se. Fourier transformation infra-red spectroscopy was used to identify the functional groups, to evidence the presence of the stabilizers, and to characterize the interactions between the nanoparticles and the stabilizer. In both cases the measurement evidenced the presence of the stabilizers, meanwhile the peak shifts mean that there is an interaction between the nanoparticles and the stabilizer mainly by OH groups.

In further experiments we would like to do biological tests to examine the uptake of the nanoparticles by plants and determine the composition of the samples.

## ACKNOWLEDGEMENT

P. Á.: Supported by the ÚNKP-19-3 new national excellence program of the ministry for innovation and technology.



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