



## ATOM-ABSORPTION METHOD OF DETERMINATION OF SELENIUM CONTENT IN SOME RAW MATERIALS AND FOOD

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**Abstract:** A novel atom-absorption method of determination of selenium in some raw materials, biological objects and food is proposed. This method involves preliminary extraction and concentrating of the components to be analyzed with butylacetate/sodium diethyldithiocarbamate mixture. The highest extraction degree for Se(IV) and Se(VI) ions is reached for pH ranged from 1 to 6. Investigation of influence of high concentrations of iron and zinc on accuracy of the Se determination proved only insignificant (under 5%) blurring of the Se atom-absorption peaks for Zn admixture contents 0÷6 g/kg and 0÷10 g/kg of Fe.

**Keywords:** Selenium; atom-absorption analysis; environmental objects; food

### 1. Introduction

Selenium and its compounds are known as biologically active and important components with clear limits of toxicity, sufficient and insufficient supply. Toxic concentration of Se disturbs normal functioning of the cell structures through formation of stable and reactionless compounds of Se and S. Selenites are easily reducible and can form free Se followed by active reactions between Se and organic compounds and its incorporation in the structure of proteins. Some authors report higher content of Se found in malignant tumours. Other results prove radioprotection activity of the low-concentrated Se and some counteraction to negative effects of the heavy metals and irradiation after treatment with the Se microdoses. Therefore, it is essential to find the clear limits between useful microdoses and harmful overdosage of this element. This issue is related to various methods available for continuous and pre-

cise analytical determination of Se content in environmental objects and other materials.

A series of experimental methods are available for experimental determination of Se content in water [1, 2], biomaterials [3], blood plasma and serum [4, 5] and food [5, 6]. However, all these methods are very complex and require deficient and expensive reagents and equipment. On the other hand, sensitivity and accuracy of some of these methods seem insufficient.

Our investigation deals with development of the quantitative determination of Se content in the above objects using a method of the extraction concentrating of Se followed by the atom-absorption spectroscopy determination of this element at the acetylene-air atomizer.

### 2. Experimental and Methods

Dithiocarbonates and dithizone are used traditionally as extraction agents [7] and

chloroform, tetrachlorated carbon, various mixtures of the polar oxygen-containing and non-polar oxygen free liquids [8] are used as organic solvents for preliminary extraction of Se from aqueous solution required for spectral determination methods. However, most of the above mentioned organic agents can complicate fine analytical determination of Se since they are hardly combustible and form yellowish and smoking flame. Besides, emission of harmful products is an unavoidable result of combustion of the chlorine-containing compounds.

Methylisobutylcetone (MIBC) is proposed in [9] as an alternative solvent. However, this agent cannot ensure sufficient concentrating degree.

In our experiments, we used the butyl ether of acetic acid as a solvent. Physico-chemical properties of this compound are similar to MIBC while concentrating performance is significantly higher.

Technically, all extractions have been performed in two systems: butylacetate/sodium diethyldithiocarbamate and butylacetate/dithizone.

Extraction mixtures have been prepared using the 10 % aqueous solution of sodium diethyldithiocarbamate and 0.01 M solution of dithizone in butylacetate.

A series of the model solutions with predetermined contents of Se has been prepared. All concentrations of Se were ranged within the values expected in real analytical samples. These solutions were prepared from the deionized water and analytically pure selenium acid. Hydrochloric acid and analytically pure ammonium solution were used to adjust pH of the systems.

A process of extraction was performed according to [10].

The flame atom-absorption spectrophotometer C-115-M1 has been used for determination of Se content. The stage of atomization was realized with the acetylene-air flame at the temperature up to 2600 °C.

A high frequency gas discharge tube filled with microamount of Se was used as a source of the discrete spectrum. All atom absorption determinations were performed at the wave length  $196.1 \pm 0.4$  nm. Rest of the samples preparation stages were made according to [11].

### 3. Results and Discussion

First, we had to select the most effective atomization mode and a value of electric current of the gas discharge tube. The mode of atomization had to provide the highest values of the wanted signal and signal/noise ratio. Results of the atomization mode selection are shown in Fig. 1.

As seen in Fig. 1, the most optimal composition of the combustible mixture can be reached at feeding the system with acetylene at the pressure  $0.4 \text{ kg/sm}^2$  and air at  $0.75 \text{ kg/sm}^2$ . This composition of the combustible mixture insures the highest and comparatively stable value of the wanted signal (light absorption value).

A dependence of the wanted signal value on the tube current is shown in Fig. 2. It can be seen that the highest wanted signal was obtained at the lowest current value (90 mA). However, under this current we had to feed the photocell with almost the highest possible current, which caused generation of quite intense 'noise'.

Taking into account the above conditions, we set the photocell feeding current value at 100 mA. This value was still close to the most optimal wanted signal area and did not cause generation of excessive interfering noise. This mode of the gas discharge tube feeding was realized using the super-high frequency electric generator 2PBL-3MV. It was also found that the hollow cathode tube produced less relevant results. At the next stage we analyzed a character of influence of pH on the Se extraction degree. A series of extractions has been performed for solutions with predetermined

content of  $\text{SeO}_3^{2-}$ . Then the content of the extracted Se in the organic phase has been determined using similar atom absorption method and the degree of absorption (R) was calculated using the formula below:

$$R = (C_0 V_0 / C_B V_B + C_0 V_0) \cdot 100 \%,$$

where  $V_0$  and  $V_B$  – volumes of the aqueous and organic phases;  
 $C_0$  and  $C_B$  – concentrations of Se in the aqueous and organic phases respectively.

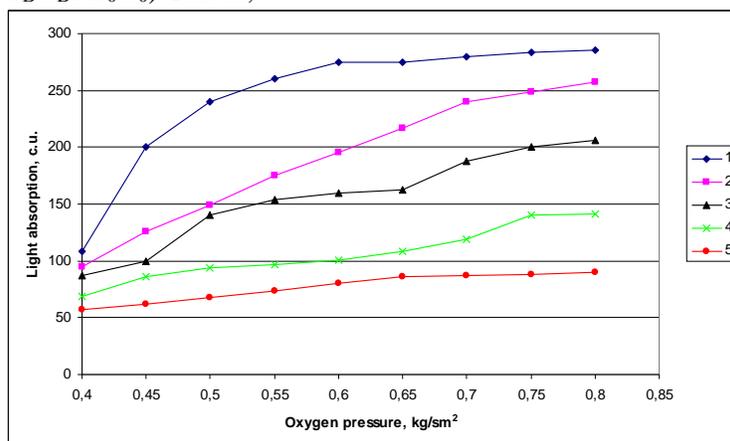


Figure 1. A series of dependencies of the light absorption (conventional units, c.u) on the oxygen pressure ( $\text{kg}/\text{sm}^2$ ) for the following acetylene pressures:  $P_{ac} = 0.40 \text{ kg}/\text{sm}^2$  (curve 1);  $P_{ac} = 0.45 \text{ kg}/\text{sm}^2$  (curve 2);  $P_{ac} = 0.50 \text{ kg}/\text{sm}^2$  (curve 3);  $P_{ac} = 0.55 \text{ kg}/\text{sm}^2$  (curve 4);  $P_{ac} = 0.60 \text{ kg}/\text{sm}^2$  (curve 5).

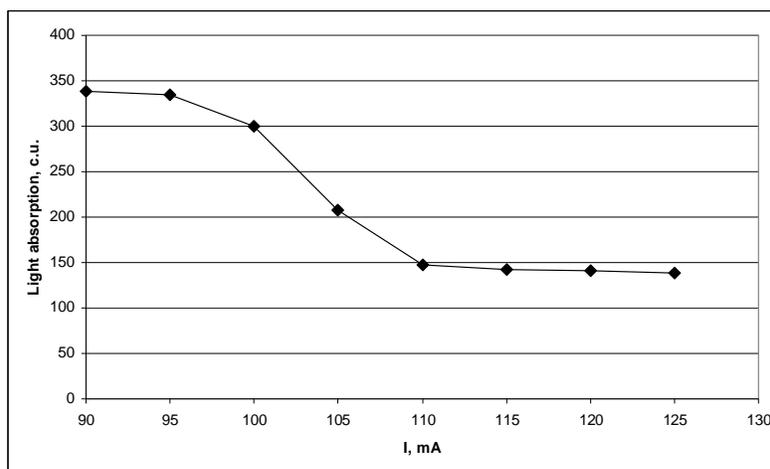
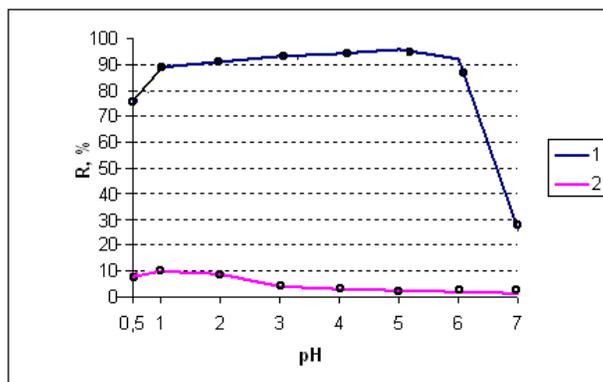


Figure 2. Dependence of the wanted signal value on the tube feeding current.

It should be noted that accurate determination of Se distribution ratio between the phases was quite difficult due to very low initial concentration in the aqueous phase. A dependence of the distribution ratio values on pH is shown in Fig. 3. One can see that the mixture butylacetate/sodium diethyldithiocarbamate

(Fig. 3, line 1) shows the highest extraction performance in the range of pH values 1-6 where this ratio is between 90-95 %. Extraction performance of the mixture dithi-zone/butylacetate is much lower and its highest value (about 10 %) is reached within pH range 0-1.5 (see Fig. 1, line 2).



**Figure 3. Dependence of the Se extraction ratio (R) on pH for the system butylacetate sodium diethyldithiocarbamate (line 1) and dithizone/butylacetate (line 2).**

Therefore, one can conclude that the extraction mixture butylacetate/sodium diethyldithiocarbamate ensures very high extraction ratio of Se and should be used for this purpose. The Se-diethyldithiocarbamate chelate is well soluble in butylacetate and this facilitates better atomization of the element.

The narrower pH range of the best Se extraction is 4-6 and our next experiments were performed within this range. A series of the model solutions was prepared and Se contents were ranged within the limits that can be expected for the real analytical systems.

A model solution with some predefined Se content was mixed with the extraction mixture butylacetate/sodium diethyldithiocarbamate with pH 4-6. After the extraction process completed, the organic mixture with extracted Se was analyzed at the atom-absorption spectrophotometer and the dependence of its optical density on initial Se concentration is shown in Fig. 4 (line 1).

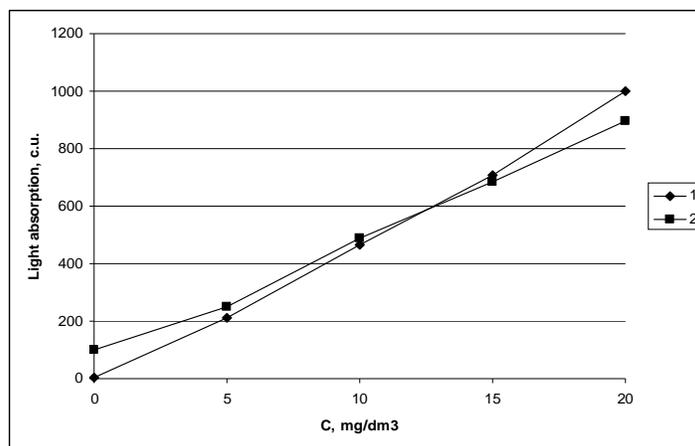
This dependence is almost exactly linear, which proves correct selection of the working concentrations range. A slope of the

line is determined by the spectrophotometer's sensitivity and in our case it seems quite sufficient for quantitative determination of the selected concentrations of Se.

It should be taken into account that many other inorganic elements would also be co-extracted from real experimental systems after their mineralization with strong inorganic acids. These side elements may significantly raise the noise level of the analytical signal complicating reliability of Se determination in the real systems.

Our next experiments were aimed onto investigation of relevance of the Se determination in more 'noisy' systems containing Se on the background of some side element(s).

A series of biological samples were mineralized and then some known amounts of selenite were added to the probes. All natural samples contain some background amounts of Se and this admixture method has to show relevance of determination of small extra amounts of Se on the background of its natural content in presence of the other elements. Results of this investigation are represented in Fig. 4 (line 2).



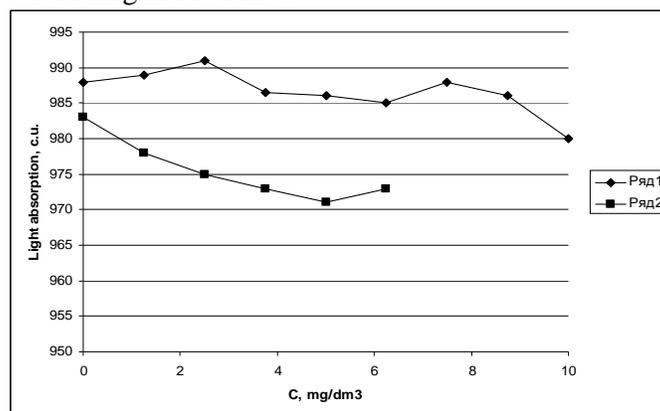
**Figure 4.** Dependence of light absorption on Se concentration in the initial model solution for extraction mixture butylacetate/sodium diethyldithiocarbamate. Line 1 – a mixture prepared with the pure deionized water; line 2 – a mixture prepared from a real biological sample with some admixture of extra selenite.

It is seen that the line 2 ('noisy' samples taken from the biological objects) is similar to the pure one (line 1) but has slightly lesser slope. This effect can be caused by influence of the 'matrix' of other elements present in the natural objects and some slackening of the wanted signal by this matrix.

It was found that the bottom limit of this method is 0.2 mg/kg Se in the organic extract. According to peculiarities of the method of the samples preparation, this concentration corresponds to the content of Se in the source biological objects or food 0.04 mg per 1 kg dry weight. This sensitivity is about one order of magnitude below

background and maximum permissible contents of Se in these objects. Therefore, this analytical method can be recommended for analytical determination of Se in food and other biological objects.

As reported in [12], ions of iron, nickel, magnesium and zinc can also be intensively co-extracted by the mixture butylacetate/sodium diethyldithiocarbamate in the weakly acid medium. Many biological objects can release significant amounts of these ions so, it is essential to investigate possible overlapping and shadowing of the wanted signal because of presence of these ions.



**Figure 5.** Influence of iron (line 1) and zinc (line 2) on light absorption of the test solution with the constant concentration of Se.

Influence of ions of iron and zinc on the wanted signal value at the given (unchanged) concentration of Se is represented in Fig. 5. We ranged contents of the both interfering elements from 0 to 6 g/kg (Zn) and 10 g/kg (Fe). It should be understood that such concentrations are about 100 times higher than the concentrations found usually in any real extractions taken from the biological objects.

It can be seen that despite some decrease of the analytical signal it remains quite strong and easily detectable. Maximum slackening of the wanted signal does not exceed 1-2 % of its value.

Such high selectivity is caused by absence of any characteristic lines close to 196.1 nm (Se characteristic line of light absorption) in the spectra of Fe and Zn. The spectrophotometer is equipped with precision

monochromator that allow to distinguish the lines with accuracy up to 0.4 nm.

Then the calibration line (Fig. 4, line 2) was employed to recalculate results of determination of Se content in a series of the soil samples taken from the grass cover in a park located in Chernivtsi, Ukraine. In order to assess relevance and accuracy of the method each sample has been analyzed in a row of 5 consequent tests. Results of the Se content determination are shown in Table 1.

As seen, statistical relevance of the atom absorption determination of Se content is quite high. Relative error of the method is 1.26-4.47 %, statistical dispersion of the results is ranged from  $1.7 \cdot 10^{-4}$  to  $3.68 \cdot 10^{-3}$  within the confidence interval 0.0334 - 0.0697.

Table 1  
Results of the atom absorption determination of Se content in the soil samples

Added selenium. mg/kg	Determined selenium. mg/kg	Relative error. %	Statistical dispersion	Average* experimental content of Se (mg/kg)
0.40	0.395 0.418 0.408 0.384 0.398	1.4	$1.678 \cdot 10^{-4}$	$0.4006 \pm 0.0334$
0.80	0.792 0.792 0.808 0.812 0.806	4.47	$9.79 \cdot 10^{-4}$	$0.802 \pm 0.0359$
1.20	1.26 1.14 1.10 1.14 1.18	2.33	$3.68 \cdot 10^{-3}$	$1.164 \pm 0.0697$
1.60	1.64 1.58 1.48 1.48 1.52	1.39	$2.325 \cdot 10^{-3}$	$1.54 \pm 0.054$
2.0	2.0 1.92 1.86 1.92 1.88	1.26	$2.88 \cdot 10^{-3}$	$1.916 \pm 0.062$

$$* \bar{x} \pm \frac{t_{\alpha} \cdot S}{\sqrt{n}}$$

#### 4. Conclusion

It can be concluded that the method of the atom absorption determination of Se with preliminary extraction by the butylacetate/sodium diethyldithiocarbamate mixture proves high relevance and accuracy and can be recommended for monitoring of content of this metal in food and other biological objects. This method is characterized by high selectivity and relatively low errors even for the 'noisy' samples containing some side elements.

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