Research Article
Hittite Journal of Science and Engineering, 2023, 10 (2) 185–191
ISSN NUMBER: 2148–4171
DOI: 10.17350/HJSE19030000306

Determination and Speciation of Selenium in Pharmaceutical Samples, Spiked Veterinary Drug Samples with a Kinetic Catalytic Method

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Article History:
Received: 2023/03/08
Accepted: 2023/05/08
Online: 2023/06/30

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This article has been checked for similarity.

ABSTRACT

In the present study, a new kinetic catalytic method was developed for the sensitive determination of selenium in pharmaceutical formulations. The reaction between basic blue 3 (BB3) and sulfide catalyzed by Se(IV) in the presence of acetic-phosphoric-boric acid buffer system. The decrease in the absorbance at 654 nm indicated the reduction of BB3. The presence of selenium(IV) accelerated the reaction rate. The method is based on the linear correlation between the amount of Se(IV) and the reaction rate. Under optimum conditions, the linear calibration range was found to be 0.1-2.0 μg ml^{-1} by the 0.5-5 min fixed time method. The tolerance limits of various species were also studied. The interfering effect of some cations, such as Cr^{3+}, Fe^{3+}, and Hg^{2+} was reduced by using cation exchange resin. The proposed method was successfully applied to spiked nasal spray and veterinary drug samples. Besides, total selenium, Se(IV) and, Se(VI) speciation were also conducted with reducing Se(VI), to Se(IV) by HCl in the synthetic mixtures.

Keywords:
Selenium, Pharmaceutical samples, Veterinary drug

INTRODUCTION

Selenium is one of the microelements that plays a role in the development and growth of mammalian organisms. Taking 55 μg/d for women and 70 μg/d for men is recommended daily. Over 800 μg/d causes toxic effects, while less than 20 μg/d causes deficiency symptoms (1). It has been reported that nearly one billion people worldwide suffer from selenium deficiency due to low-selenium-containing foods (2). Therefore, it is important to supplement feeds and foods with selenium.

There are quite several instrumental techniques for the determination of selenium given in the literature, some of which are highly sophisticated: spectrofluorimetry (3), electrothermal atomic absorption spectrometry (4, 5), hydride generation (6), ICP AES (7), cathodic stripping voltammetry (8-10), anodic stripping voltametry (11), radiochemical neutron activation analysis (12-15) high performance liquid chromatography (16, 17), ICP MS (18), particle beam/hollow cathode optical emission spectroscopy (19), and flow-injection techniques (20, 21).

Kinetic catalytic analysis methods are one of the most functional and economical methods used for a long time. The amount of catalyst can be determined where a catalyst accelerates the reaction rate. The method's selectivity is directly proportional to the selectivity of the catalyst to the reaction. Various instrumental devices can monitor the reaction rate in these methods. The fact that it usually does not require sophisticated equipment and is relatively low in cost makes the technique widespread.

Several indicator reactions are known (tab. 1) for the determination of selenium by the kinetic method with low detection limits. These methods have been developed because the amount of selenium changes the reaction rate linearly. (22).

In the present study, an easy, economically feasible, sensitive spectrophotometric method for quantitative analysis of selenium at μgml^{-1} level was developed. The procedure is based on the linear response of selenium concentration due to its catalytic effect on a redox reaction between BB3 and sulfide. The method was successfully applied to selenium-spiked nasal spray samples and veterinary drugs. To ensure the method's selecti-

Cite as:
Bagda E. Determination and speciation of selenium in pharmaceutical samples, spiked veterinary drug samples with a kinetic catalytic method. Hittite J Sci Eng 2023;10(2):185-191. doi:10.17350/hjse19030000306

vity, parameters affecting the reaction rate, such as pH, buffer amount, temperature, and reagent concentrations, have been investigated and optimized. The analytical properties of the proposed catalytic kinetic reaction were strictly controlled to determine Se(IV) in pharmaceutical preparations accurately.

Table 1. Some existing kinetic methods for determination of selenium.

Indicator system	Se species	Linear range	Analitical application(s)	Remarks	Ref.
Spands-S^{2-}, CPC	Se(IV)	0.5-100 ng ml^{-1}	Real and synthetic water samples	Many cations interfere such as Mg (II), Fe (III), Zn (II) at only1 fold.	23
IC- S^{2-}	Se(IV)	50-400 µg L^{-1}	Tablets	Interfering heavy metal ions can be masked with EDTA.	24
HD-bromate-Ponceau S	Se(IV)	No need to find linear range	Water samples	As (III) interferes at even 1 fold.	25
DMPA-MB	Se(IV)	0.9-9.6 ng ml^{-1}	Natural waters	Cu (II) interfered even in comparable amounts.	26
Fe(II)-EDTA	Se(IV)	0.2-2 ng ml^{-1}	Water samples	Reducing agents and oxidants interfere.	27
p-CPF-bromate	Se(IV)	0.4-15 µg L^{-1}	Foodstuff samples	Interfering ions can be eliminated by SDG.	28
HD-bromate Ponceau S	Se(IV)	4.5-400 ng ml^{-1}	Water, tablet, shampoo	Interfering ions can be eliminated by acidic ion exchange resin or extraction with chloroform.	29
EDTA-nitrate-amonium iron(II) sulphate	Se(IV)	$5x10^{-9}$-$2x10^{-7}$ and $2x10^{-7}$-$2x10^{-6}$ g L^{-1}	Seawaters	Cu^{2+}, Fe^{3+}, Fe^{2+} interfere seriously.	30
S^{2-}-BB3	Se(IV), Se(VI) and total Se	0.1-1.1 and 1.1-2.0 µg ml^{-1}	Spiked nasal spray, veterinary drugs	Interfering ions can be eliminated by cationic exchange resin.	This work

CPC: Cetyl pyridinium chloride, IC: Indigo carmine, HD: Hydraziniumdichloride, DMPA:2,3 dimethylmercaptopropionic acid MB: Methylene blue, SDG: Sulphydryl dextrane gel, EDTA: Ethylene diamine-tetra asetic acid, MO: Methyl orange, BB3: basic blue 3

MATERIAL AND METHODS

Absorption measurements at λ_{max} 654 were performed with Shimadzu UV 1800 spectrophotometer. Sartorious basic pH meter used to adjust the pH of buffer solutions. After cleaning all the glassware, they were kept in HNO_3 (5%) and washed again with double distilled water (DDW). All chemicals used are of analytical purity. Nitrate salts of cations and sodium or potassium salts of anions were used for interference studies.

Stock basic blue 3 solutions were prepared in DDW. The buffer solutions (pH: 4.0-9.0) were prepared from boric- phosphoric-acetic acid solutions (0.04 M of each) and sodium hydroxide (0.2 M).

Stock Se(IV) solution was prepared from Na_2SeO_3 and sulfide from $Na_2S.9H_2O$ in DDW. This sulfide solution was prepared freshly before use. 1% of ethylenediaminetetraacetic acid solution was prepared from Na salt of EDTA.

Recommended Procedure for Se (IV)

The rates of the kinetic reaction and the reaction catalyzed with Se(IV) were followed spectrophotometrically between 0.5 to 5 minutes (λ_{max}=654 nm).

Appropriate amounts of Se(IV) solution, 1.0 ml EDTA (1%), 1.0 ml Na_2S (0.1 M), 3 ml buffer, and 130.0 µL BBY solutions were mixed with distilled water to 10.0 ml. The absorbance value at 654 nm was followed in the 0.5-5 minutes range. All experimental procedures were also applied to selenium-free solutions. In this way, the rate of the uncatalyzed reaction was also followed.

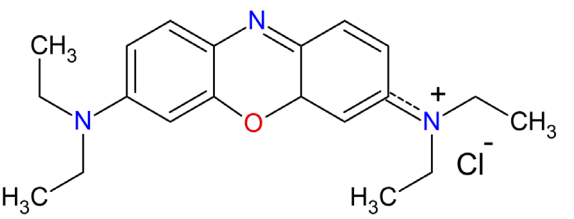

Figure 1. Chemical structure of Basic blue 3

RESULTS AND DISCUSSION

As stated in the literature, selenium is essential for the systemic functioning of the organism, and its useful range is narrow and excessive exposure can cause adverse effects (31). So, the determination of selenium in different matrices is an important task.

Since BB3 has delocalized π electrons, it has strong adsorption in the visible region. The reduction of this dye with sulfide takes place at room temperature, and trace amounts of selenium (IV) catalyze the reaction. Reduction of BB3 ca-

uses a decrease in absorbance at λ_{max}. Se(IV) accelerates this reduction as it catalyzes the reaction. Therefore, following the reaction rate allows the determination of Se(IV). The proposed mechanism according to the literature is (32, 33):

$$2BB3^{+} + S^{2-} + 2H_2O \rightarrow 2HBB3^{+} + 2OH^{-} + S \text{ (slow)}$$

In the presence of excess sulphide $S + S^{2-} \rightarrow [S...S]^{2-}$

In the presence of Se(IV) selenosulfide, $[S...Se]^{2-}$, forms

$$2BB3^{+} + [S...Se]^{2-} + 2H_2O \rightarrow 2HBB3^{+} + 2OH^{-} + S + Se$$

EDTA was used due to its masking ability of many cationic species. EDTA can be complex with cations and may reduce their interfering effect. Besides, the experimental data show that the reaction between BB3-sulfide accelerated up to 0.04 % EDTA concentration in the presence of selenium, so EDTA behaves as an activator in the reaction medium.

Effect of Reaction Parameters

The difference in the reaction rates between the reactions with and without selenium (IV) is important for the sensitivity of my method. At the same time, the selectivity of the process should be high. Optimizing the parameters affecting the reaction is very important for the proposed kinetic catalytic method to have maximum sensitivity and selectivity and to obtain reproducible results. Therefore, all experimental parameters were optimized individually, keeping all other variables constant.

The optimum values are chosen to have the maximum net reaction rate (ΔΔA) and to have reproducible results.

Influence of pH

The influence of pH on the redox reaction rate was studied over pH 4.0-9.0. The rate of both redox reactions with and without selenium (IV) decreased up to about pH 6.0, and then both reactions almost stopped and reached a plateau (Fig.2). The difference between rates of reactions with and without Se(IV) had the maximum value at pH 5.0. Hence, the optimum pH of the system was chosen as 5.0.

Influence buffer volume

The buffer volume's influence on redox reactions was investigated in the 1.0-7.0 ml range. The results (Fig. 3) showed that the rate of both reactions with and without Se(IV) was increased with buffer volume up to about 5.0 ml. In the same way, the sensitivity of the reaction had a maximum value of 5.0 ml. Thus a buffer volume of 5.0 ml was chosen.

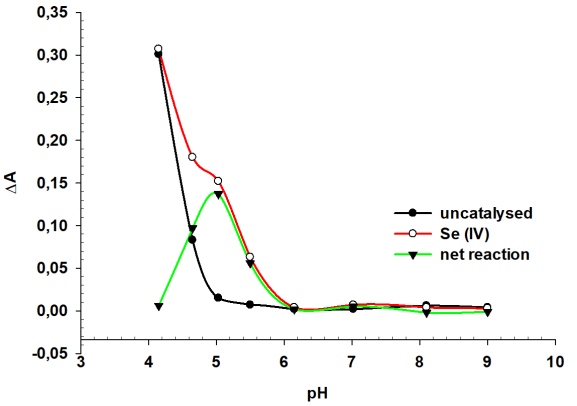

Figure 2. Optimization of pH (buffer volume: 5.0 ml, [BB3]: 1.45 x 10^{-5} M, [S^{2-}]: 0.01 M, 25 °C).

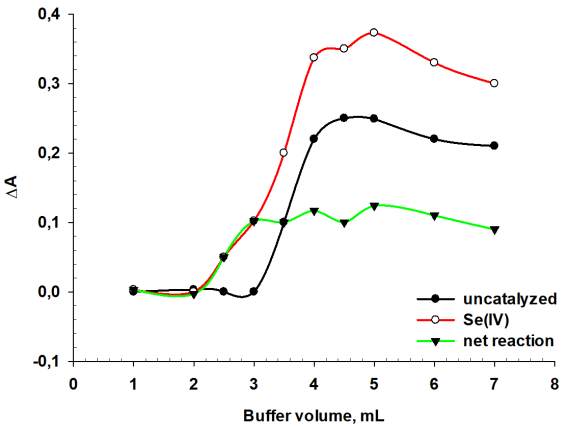

Figure 3. Optimization of buffer volume (pH: 5.0, [BB3]: 1.45 x 10^{-5} M, [S^{2-}]: 0.01 M, 25°C).

Influence of BB3 concentration

The influence of BB3 concentration on the catalyzed and uncatalyzed reaction rate was studied over 4.0 x 10^{-3}-8.0 x 10^{-3} mg ml^{-1} range. As shown in Figure 4, the catalyzed reaction rate decreased gradually with increasing concentration of BB3. The value 5.2 x 10^{-3} mg ml^{-1} (1.45 x 10^{-5} M) was chosen (the optimum value that the reaction did

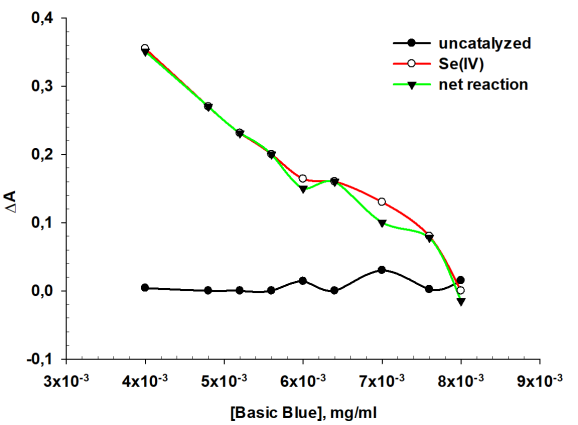

Figure 4. Optimization of dye concentration (buffer volume: 5.0 ml, pH: 5.0, [S^{2-}]: 0.01 M, 25°C).

not end in the duration of kinetic measurements).

Influence of sulfide concentration

The influence of sulfide concentration on redox reaction was investigated between the range of 3.0 x 10^{-3}-1.5 x 10^{-3} M (Fig. 5). The presence of sulfide increases the reaction of both reactions with and without selenium (IV). The sulfide concentration of 0.01 M was adopted. Because, at concentrations below the optimum value, the decolourization rate of the solution was too slow to follow, and at higher concentrations, rate of reaction measurements have low reproducibility.

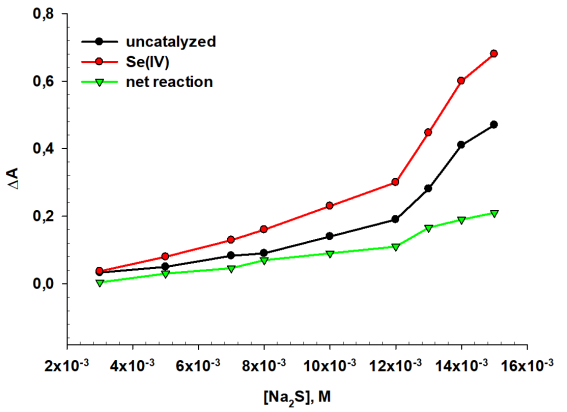

Figure 5. Optimization of reducing agent concentration (buffer volume: 5.0 ml, pH: 5.0, [BB3]: 1.45 x 10^{-5} M, 25°C).

Influence of temperature

The effect of temperature on the reaction rate between 25.0-55.0 °C was investigated because it can seriously change the reaction rate. Increasing the temperature of the reaction medium increased the reaction rate both in the presence and in the absence of selenium. Especially for the reactions with and without selenium above 45.0 °C, the ΔA values were very close to each other. This was due to the fact that the temperature increased the reaction rate even in the absence of a catalyst. Thus the ΔA values and sensitivity of the whole system decreased from these values. 25.0 °C was chosen as optimum for its easy control.

Analytical Parameters

The absorbance for net reaction (Δ (ΔA)) was linear for 0.5-5 min with the equation and range given method:

Δ (Δ*A*) = 0.316$C_{Se(IV)}$- 0.011 for the range 0.1-1. 1 μg ml^{-1} (r^2=0.9928, n=3), 3 S_b/m=0.030, 10 S_b/m= 0.099

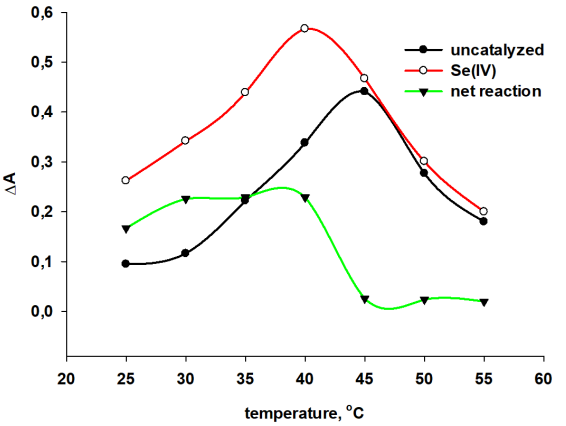

Figure 6. Optimization of temperature (buffer volume: 5.0 ml, pH: 5.0, [BB3]: 1.45 x 10^{-5} M, [S^{2-}]: 0.01 M, 25°C).

Δ (Δ*A*) = 0.276$C_{Se(IV)}$- 0.211 for the range 1.1-2.0 μg ml^{-1} (r^2=0.9903, n=3), 3 S_b/m=0.034, 10 S_b/m= 0.114

The calibration range was found between 0.1-1.1 μg ml^{-1} with regression coefficient (r2) of 0.993, and in the range 1.1-2.0 μg ml^{-1} with r^2 of 0.990 where $C_{Se(IV)}$ is the concentration of selenium in μg ml^{-1} and Δ(Δ*A*) is the difference of "absorbance difference" in the presence and absence of selenium (IV). The limit of detection ($3S_b$/m) was 0.030 and $10S_b$/m was 0.099 μg ml^{-1} in the range 0.1-1.1 μg ml^{-1} and $3S_b$/m was 0.034 and $10S_b$/m was 0.114 μg ml^{-1} in the range 1.1-2.0 μg ml^{-1} where the S_b stands for the standard deviation of signal blank solution and m is stand for the slope of the calibration curve.

Selectivity of the Basic blue 3 and sulfide reaction

A series of samples containing interfering species and 0.6 μg ml^{-1} of Se (IV) were prepared to test the selectivity of the developed method to selenium. The interference effect was investigated by monitoring the reaction rates of these samples and the samples containing only selenium. The interfering ion's maximum concentration, which caused a ±5% relative error in determining Se (IV), was defined as the tolerance limit (table 2).

As can be seen from the table, even the presence of common ions such as Na^+ and K^+, 2000 times more could be tolerated. On the other hand, the interference of rarer species, such as mercury vanadium (V^{5+}, Hg^{2+}), has been greatly improved by using resin.

The analytical properties of the proposed method

It is very important to do accuracy and precision studies to determine the analytical features of the method. For this purpose, the proposed method determined selenium

Table 2. Effect of various ions on the determination of 0.6 µg ml-1 of Se (IV) at the optimum conditions.

Foreign ion	Tolerance limit, [Interfering ion/ Se(IV)]	Tolerance limitb, [Interfering ion/ Se(IV)],
Na^+, CH_3COO^-, HCO_3^-, K^+, Cl^-,	2000[a]	-
Zn^{2+}, Ba^{2+}, Co^{2+}, Sr^{2+}, Ni^{2+}, Mn^{2+}, Al^{3+}, Cu^{2+}, SO_4^{2-},NO_3^-	1000	-
Ca^{2+}, Cd^{2+},NH_4^+, Li^+	600	-
F^-, PO_4^{3-}, IO_3^-	150	
$Cr_2O_7^{2-}$, Cr^{3+}	100	500[a]
Se(IV) ,Fe^{3+}	50	500[a]
V^{5+}, Hg^{2+}	<1	100

[a]largest amount tested, [b]After using Dowex 50 W X 8-100

concentrations of synthetic samples containing different amounts of Se(IV); the results are given in Table 3. The recovery and rsd % values were found to be satisfactory.

Table 3. Accuracy and precision of the BB3-sulfide method, (n=5)

Se (IV) µg ml^{-1}		Recovery	%RSD
Present	Found±SD		
0.200	0.197±0.010	98.5	5.08
0.400	0.396±0.017	99.1	4.29
0.600	0.598±0.029	99.7	4.85
1.200	1.250±0.049	104.2	3.92
1.600	1.629±0.079	101.8	4.85
1.800	1.760±0.090	97.8	5.11

%RSD: relative standard deviation

The analytical applications

Determination of selenium in nasal spray samples

The applicability of the BB3-sulfide method is also conducted with the determination of selenium for selenium spiked nasal spray sample, sterile isotonic seawater solution (Tonimer Baby, Berko Pharmaceuticals.). An aliquot of selenium (IV) solution was spiked to 10.0 ml of spray solution, the solution was passed through cation exchange resin, and the final solution was diluted to 25.0 ml with DDW (tab. 4).

Determination of selenium in veterinary formulations

Determination of selenium (IV) in the veterinary formulation was conducted using the method given by Zaporozhets et al. (30). Appropriate amounts of veterinary drug powder or solution samples were dissolved in 40.0 ml of DDW, and suspended particles were removed by filtration after centrifugation of the solution at 5000 rpm for 5 minutes. The solid residue was washed twice with DDW; all portions of the solution were collected and diluted to 100 ml with DDW (tab. 5).

Table 4. Determination of selenium in nasal spray sample, (n=5).

Se (IV) µg ml^{-1}		Recovery	%RSD
Added	Found		
-	BDL	-	-
0.200	0.216	108	4.19
0.400	0.376	94.0	4.85
0.600	0.629	105	4.72
1.100	1.118	102	5.15
1.500	1.473	98.2	3.27
1.800	1.837	102	4.51

Table 5. Determination of selenium in veterinary formulations, (n=5).

Veterinary Formulation	Se (IV) µg ml^{-1}		Recovery	%RSD
	Present	Found		
Evit Se	9.1	8.8	96.7	5.4
Selephose	9.3	9.7	105	5.2
Yeldif	9.1	8.4	92	8.0

Selenium (IV) and (VI) speciation studies

In order to determine the Se(IV) and Se(VI) content of synthetic solutions four, different synthetic solutions containing varying amounts of Se(IV) and(VI) were prepared (tab. 6). The Se(IV) content of the solutions was determined with the proposed method without any pretreatment. On the other hand, the Se(VI) content was determined after the reduction of Se(VI) to Se(IV). The difference between total selenium and Se(IV) was equal to the content of Se(VI). The reduction was carried out as follows:

Table 6. Se (IV) and Se (VI) speciation results.

Sample	Added, µg ml^{-1}		Found, µg ml^{-1}	
	Se (IV)	Se (VI)	Se (IV)±SD	Se (VI) ±SD
SS1*	0.100	0.400	0.097±0.004	0.411±0.020
SS2	0.400	0.100	0.378±0.019	0.102±0.008
SS3	1.500	0.200	1.572±0.071	0.187±0.009
SS4	0.200	1.500	0.209±0.011	1.611±0.084

*SS: Synthetic sample, ±SD: standard deviation

25 ml of synthetic solution was mixed with 5.0 ml of concentrated HCl and heated for about three hours. The resulting solution was diluted to the appropriate volume with DDW to protect the pH meter probe. The pH of the solution was adjusted to 6-8 with NaOH solution.

CONCLUSION

The proposed method is based on the catalytic effect of

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Se(IV) on the reduction of BB3 by sulfide. Due to the linear relationship of the reaction rate with the amount of selenium, the method is linear in the range of 0.1-2.0 μg ml^{-1}. The method is an easy method to implement and does not include laborious and time-consuming preparation steps. In addition, expensive chemical reagents and sophisticated instrumental devices are not required to perform the method. The method was successfully applied to the determination of spiked nasal spray samples and veterinary drug samples. The data obtained from speciation studies was also satisfactory.

CONFLICT OF INTEREST

The author declares no conflict of interest.

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