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Determination of trace amounts of selenium in natural spring waters and tea samples by catalytic kinetic spectrophotometry

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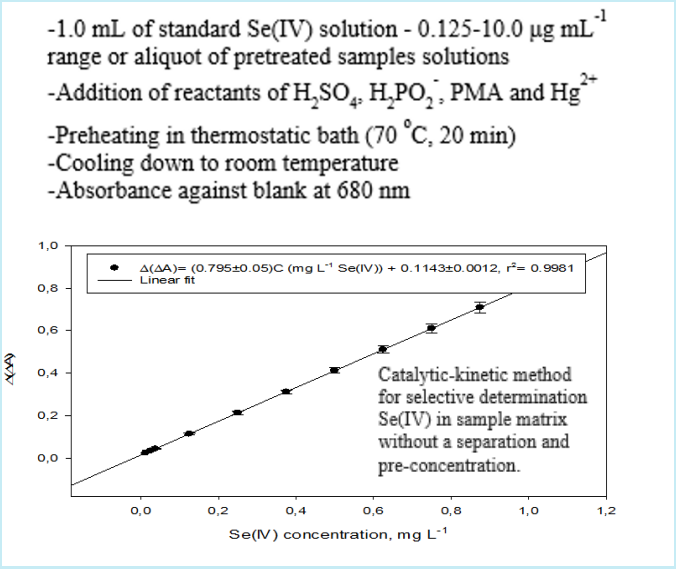
ABSTRACT: In this work, a new kinetic method is described for the determination of trace Se(IV) in natural spring waters and commercial tea samples. The method is based on the activation of Se(IV) onto the indicator reaction in acidic medium. The reaction was monitored using a fixed time approach of 20 min at 680 nm. The variables affecting the reaction rate were evaluated and optimized. The method allows the determination of Se(IV) in the range of 0.0125-1.0 mg L^{-1} with a detection limit of 3.6 µg L^{-1}. The precision was in range of 0.63-3.15% (as RSD %) with a higher recovery than 98.6%. The method has been found to be selective against matrix effect. The method was applied to the speciation analysis of inorganic Se species present in the selected samples. The method was statistically validated by analysis of two certified samples and comparing the obtained results to those of HG-AAS analysis. Also, the total Se levels of the samples were determined by using both methods after conversion of Se(VI) into Se(IV) in ultrasonic bath in acidic medium for 30 min at 85-90 °C. The results were in good agreement with those of HG-AAS. The Se(VI) level of the samples was calculated from the difference between amounts of total Se and Se(IV).



1. Introduction

Selenium is an essential trace element with only a small difference between toxic and essential levels. It has been reported that selenium has an anticancer effect, protecting the human body from free radicals and preventing heavy metal toxic effects[1], but it is also a potential toxicant[2]. Selenium concentration in fresh waters is usually around 20 µg L^{-1}. The selenium content of surface waters is greatly influenced by pH, being high in acidic (pH < 3.0) and in alkaline waters (pH > 7.5). Traces of selenium ranging from 0.01 to 10 µg L^{-1} are commonly found in community drinking water. The guideline level of selenium in drinking water set by the World Health Organization (WHO) was 10 µg L^{-1} [3]. As bioavailability and absorption strongly depend on chemical form in which the element is present, rapid, accurate and precise analytical methodologies for the qualitative and quantitative speciation analysis of selenium in foodstuffs are now becoming more and more necessary[4]. In addition to food, beverages may act as another important potential ingestion way to elements in our daily life[5]. As a popular nonalcoholic and healthy beverage, tea is massively consumed in the world[6]. The regular consumption of tea may contribute to the daily

dietary requirements of several essential elements. Considering the enormous consumption of tea and the investigation focusing on selenium, there is great importance to study inorganic selenium speciation in tea samples as well as in natural waters[7].

There are many analytical techniques with their self-advantages and disadvantages, such as capillary electrophoresis online coupled with hydride generation-atomic fluorescence spectrometry (CE/HG AFS)[2], inductively coupled plasma mass spectrometry (ICP MS) after a separation and preconcentration procedure[4,7], spectrophotometry with and without preconcentration[8,9], graphite furnace atomic absorption spectrometric (GF AAS) after preconcentration with coprecipitation[10], electrothermal atomic absorption spectrometry (ET AAS)[11], inductively coupled plasma optical emission spectrometry with hydride generation (HG ICP OES)[12], atomic absorption spectrometry with hydride generation (HG AAS)[13], and high performance liquid chromatography with UV detection (HPLC)[14-17] in literature for speciation analysis of inorganic selenium species.

In routine analysis, the spectrophotometric method is a versatile and cost-effective analytical tool that is easy to use, simple and requires no expert user in this area for underdeveloped and developing countries. However, the above-mentioned methods are time-consuming or less sensitive. Catalytic kinetic methods are noteworthy due to their significant advantages in determining many organic and inorganic components at trace levels without the need for prior separation and enrichment step with the choice of a good indicator, catalyst, inhibitor and activator.

Different catalytic kinetic methods have been reported for the determination of inorganic selenium species like Se(IV), Se(VI) and total selenium in waters[18-24], including micellar sensitized kinetic quantification of low levels of bisphenol A in foodstuffs by spectrophotometry[25]. Significant number of methods for the determination of selenium in real samples have been based on the catalytic effect of Se(IV) on the reduction of absorbing chromogenic or fluorogenic dyes in visible region, 380-800 nm, such as Toluidine blue[26], Methylene blue[27], Gallocyanin[28], Semicarbazite[29], and Ponceau S[30]. Some of these methods have high selection limits or suffer from many interfering species such as Te(IV) and As(V), have time-consuming and laborious processes, and at the same time these methods are unstable. There are a limited number of catalytic kinetic methods that allow the determination of Se(IV), Se(VI) and total selenium in water samples[31]. Therefore, there is still a need to develop more sensitive and selective catalytic kinetic spectrophotometric methods for the determination and speciation of selenium in real matrix samples such as natural hot springs and tea samples.

In the present study, Se(IV) was used as an activator to increase the sensitivity and stability of the indicator system, Hg(II)-PMA-NaH_2PO_2-H_2SO_4. The variables affecting the reaction rate were evaluated in detail and optimized to give the best calibration sensitivity. The developed activation-controlled kinetics system has been successfully applied to speciation analysis of the inorganic selenium species present in natural spring water and tea samples. The proposed kinetic method is sufficiently sensitive, selective, very simple and practical to use. The existing kinetic method, without any pre-separation and enrichment, is as accurate and reliable as the sensitive and element selective HG AAS, which is commonly used for selenium analysis in real samples.

2. Materials and methods

2.1. Instrumentation

In the present study, a spectrophotometer equipped with a 1 cm light path quartz cell (Shimadzu model UV-Visible 1601 PC, Kyoto, Japan) was used for absorbance measurements at 680 nm. A thermostatic water bath was used to control the reaction temperature with accuracy of ±0.5 °C. A stopwatch was used to record the reaction time. Shortly before the start of the indicator reaction with and without the activator, all the solutions were preheated to a temperature of 70 °C. A Sonicor model SC-121TH ultrasonic probe with total volume of 4 L was used for ultrasonic dissolution (optimal conditions, 35 kHz, 220 V, for 15 min at 65 °C). In addition, HG AAS (in terms of total Se analysis) was also used to check the accuracy of the method. For comparative purposes, the hydride for Se analysis was run with an atomic absorption spectrometer (HG AAS, Shimadzu AAS-6300, HVG-13 channels) forming under the following operating conditions: 4.0 (w/v) $NaBH_4$, 6-8 mol L^{-1} HCl, carrier argon gas at a pressure of 0.32 MPa at a flow rate of 70 mL min^{-1},

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
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air at a flow rate of 7.0 L min^{-1} for fuel/burner acetylene at a flow rate of 15 L min^{-1}, 0.2 nm bandwidth, 194.0 nm wavelength and 10 mA lamp current.

2.2. Chemicals and solutions

All chemicals used were in analytical reagent purity. 1000 mg L^{-1} Se(IV) and Se(VI) solutions were prepared by dissolving the appropriate amounts of solid Na_2SeO_3 and Na_2SeO_4 in doubly distilled water and completing with water to the line. 100 mL of 1.5 mol L^{-1} H_2SO_4 solution was prepared by diluting the concentrated solution with water. 100 mL of 0.5 (w/v) PMA solutions was also prepared by dissolving 0.5 g of solid PMA in diluted NaOH and diluting with water. 100 mL of 0.5 mol L^{-1} hypophosphite solution was prepared by dissolving suitable amounts of solid NaH_2PO_2 in water, homogenizing thoroughly with water and soaking in water. 100 mL of 0.01 mol L^{-1} Hg(II) ion solution was prepared by dissolving a known amount of solid $Hg(NO_3)_2$ salt in analytical purity in water and diluting with water. The other reagents (HNO_3, H_2O_2, HCl and 1.5% (w/v) $NaBH_4$ in 0.2% (w/v) NaOH) used in dissolution of the samples, interference studies and selenium analysis steps by Hg AAS, were used by either direct or preparing solutions at known concentrations.

2.3. Preparation of samples for analysis

Natural cold- and hot-spring water samples were directly collected from the cold and hot spring (Kalin Town, Sivas, Turkey) and stored in a cool, dark place to protect them from heat and light. Water samples were acidified using dilute HNO_3 to prevent metal ions from adsorbing on the walls of the measurement containers. Samples were passed through a 0.45 μm pore size membrane filter to remove suspended solids prior to analysis. To determine the total selenium, samples were submitted to analysis under optimum reagent conditions, without any other pretreatment, except for prereduction with HCl. Where necessary, known volumes of masking reagents such as thiourea and NH_4F were added to the solution medium prior to analysis to control possible interference resulted from Te(IV), Cu(II), Bi(III) and Sn(IV) ions. At least, one blank solution for each sample was also analyzed to evaluate metal contamination with the reagents used.

Initially, the certified tea sample (about 0.1-0.2 g) was subjected to analysis for different sonication times (5-30 min), temperature (25-80 °C) and H_2SO_4 concentration (0.2-5 mol L^{-1}) under 35 kHz ultrasonic power for the optimization of the ultrasonically assisted dissolution process. The certified value of sample was considered as base to assess the effectiveness of the procedure. Optimal values were found to be an acid concentration of 3.5 mol L^{-1}, sonication temperature of 65 °C and sonication time of 15 min after each optimization step. Real tea samples were solubilized in these conditions, converted to hydride, H_2Se after reduction with 1.5% (w/v) $NaBH_4$ in acidic medium (4.0 mol L^{-1} HCl) and detected with HG-AAS. Approximately 0.1 g of tea samples was taken in PTFE dissolution vessels for five repetitive analyzes, and each was mixed with 5 mL of concentrated acid and/or acid mixture (H_2SO_4 or H_2SO_4-HNO_3-H_2O_2, 2:2:1 (v/v)). The flasks were covered with a watch glass, and then dissolved at 60-80 °C for 3-4 h. The acid and/or acid mixtures were intermittently added until the color of the solution became transparent, and the heating was continued. The excess acid was evaporated until a semi-dried mass remained; 2.0 mL of 0.2 mol L^{-1} HNO_3 was added to this after cooling and centrifuged for 10 min at 3500 rpm. Final volume was completed to a volume of 5.0-10 mL using 0.5 mol L^{-1} HNO_3, and the known volumes of sample solution were analyzed by kinetic method. For the tea samples below the detection limit, the standard addition-based calibration curve approach was used when necessary, and the total selenium level of the sample was determined from difference after prereduction. The blank samples were analyzed in a similar way.

2.4. The catalytic kinetic procedure

A suitable volume (1.0 mL) of standard Se(IV) or sample solution in linearity range of 0.125-10.0 μg mL^{-1} was transferred to a centrifugation tube of 10 mL, and then 0.5 mL of 1.5 mol L^{-1} H_2SO_4, 0.1 mL of 0.5 mol L^{-1} $H_2PO_2^-$, 1.5 mL of 0.5% (w/v) PMA and 0.75 mL of 0.01 mol L^{-1} Hg^{2+} solutions were sequentially added. After that, the volume was completed to 10 mL with water and incubated at 70±0.5 °C for a fixed time of 20 min. The thermostat was left in the equilibrium in the water bath. Finally, the solution was brought to room temperature by holding under the running

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tap. The absorbance of the indicator solution at 680 nm for analysis of Se(IV) was measured against water using a 1-cm quartz cell and taken as an analytical signal. In a similar way, under optimal conditions, the absorbance was measured for the noncatalyzed solution without Se(IV) and the signal ΔA_C was taken into account. As a measure of calibration sensitivity, $\Delta(\Delta A)$: ΔA_C-ΔA_0 difference as a net analytical signal was plotted *versus* Se(IV) concentration, and a calibration curve was generated. The selenium contents of the samples were determined using this calibration curve.

3. Results and discussion

3.1. Absorption properties

Phosphomolybdic acid (PMA), a heteropoly acid with three acid ionization constants ($pK_{a1,2,3}$: 2.40, 4.32 and 5.46), is a dye which is commonly used for sensitive detection of low molecular mass compounds such as alkaloids, phenolic species and steroids for visualization of complex biological structures in TLC. PMA ($H_3PMo_{12}O_{40}$, FA: 1825.25 g moL^{-1}), also known as dodeca molybdic acid, is a yellowish-green compound, soluble in polar organic solvents such as water and ethanol. Conjugate unsaturated compounds reduce PMA to Mo-blue. Color intensity increases with the number of conjugated double bonds present in the dye molecule[32]. The PMA's implementation principle is based on the fact that many inorganic and organic materials form highly colored blue mixed oxide where the initial Mo(VI) is reduced to Mo(IV). Similar reaction products can be easily monitored by light and electron microscopy and can be measured by spectroscopic techniques, usually at a wavelength of 600-900 nm, depending on the nature of the reducing agent used[33,34]. Different investigators[35-41] reported different absorption spectra with different wavelengths for maximum absorption for the Mo-blue complex. In the present study, when sodium hypophosphite was used as a reducing agent for PMA, and when H_2SO_4 was added, intense blue color appeared. The shape and maximum absorption wavelength of the absorption spectra are changed by changing the concentration of acid in solution in the presence of Hg(II) and Se(IV) ions at constant concentrations. A comparison between these spectra showed that the maximum absorbance for a solution containing 0.075 mol L^{-1} H_2SO_4 in a final volume of 10 mL was observed at 680 nm. Increasing Hg(II) and Se(IV) concentrations at constant acid concentration also led to an increase in the absorbance at the characteristic absorption wavelength. For this reason, 680 nm was taken into account as working wavelength for further studies.

3.2. Indicator reaction

PMA was used as a redox indicator because of its ability to produce a product such as Mo-blue, which has a characteristic absorption effect on the visible region when reduced. Reduction of PMA in the presence of hypophosphite in acidic medium at room temperature is very slow. However, Se(IV) at trace levels activates selectively the catalytic effect of Hg(II) ions in acidic medium at 70 °C. This can be explained by the stable complex formation of Se(IV) in the catalytic cycle of Hg(II) ions in the acidic medium. According to Pearson's acid-base theory, Hg(II), which is soft Lewis acid, will interact with the soft base Se(IV) to form Hg-Se bond. The rate increase observed in the catalytic behavior of Hg(II) in the presence of trace Se(IV) was spectrophotometrically monitored at 680 nm. The catalytic reaction mechanism, based on the expected activation, can be predicted as follows:

$$H_3PMo_{12}O_{40} + 12H_2O \rightarrow 27H^+ + PO_4^{3-} + 12MoO_4^{2-} \ (pK_{a1,2,3}: 2.40, 4.31 \text{ and } 5.46) \quad (1)$$

$$2MoO_4^{2-} + H_2PO_2^- + 4H^+ \rightarrow Mo_2O_5 \times 2H_2O + H_2PO_3^- \text{ (slow, uncatalyzed reaction) Mo-blue} \quad (2)$$

$$\text{(i) } 2Hg^{2+} + H_2PO_2^- + H_2O \rightarrow Hg_2^{2+} + 2H^+ + H_2PO_3^-$$

$$\text{(ii) } Hg^{2+} + H_2SeO_3 \rightarrow Hg(SeO_3H)^+ + H^+ (pK_{a1,2}: 2.46 \text{ and } 7.30)$$

$$\text{(iii) } Hg(SeO_3H)^+ + H_2SeO_3 \rightarrow Hg(SeO_3H)_2 + H^+, \log\beta_2: 7.69 \text{ (stable complex formation)}$$

$$\text{(iv) } 2Hg(SeO_3H)_2 + H_2PO_2^- + H_2O \rightarrow Hg_2^{2+} + 2HSeO_3^- + H_2PO_3^-$$

$$\text{(v) } 2MoO_4^{2-} + Hg_2^{2+} + 6H^+ \rightarrow 2Hg^{2+} + Mo_2O_5 \times 2H_2O + H_2O$$

$$2MoO_4^{2-} + H_2PO_2^- + 4H^+ \rightarrow Mo_2O_5 \times 2H_2O + H_2PO_3^- \quad (3)$$

(Fast, catalyzed reaction in presence of Se(IV)) at 680 nm.

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
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3.3. Optimization of the analytical variables

The effect of reaction variables (acidity, concentration of reactants, temperature, time, and ionic strength of the medium) on the net reaction rate was extensively evaluated and optimized by monitoring each variable at a certain interval by keeping all other variables constant, based on optimization tool which is also well-known as univariate approach. In fact, in which there is not an interaction between variables, this approach is simpler, easy to use, more reliable, and moreover does not require an expert user (herein, a mathematician or statistician, which can statistically use multivariate models in optimization step) in his/her area to determine whether or not a variable is significant, and to establish relationships between variables as only one variable is used each time to obtain results. The optimum values of the variables for triplicate measurements of selenium at fixed concentration of 0.25 mg L^{-1} were determined to obtain the minimum detection limit and maximum sensitivity at each determination. The results were represented as error bars showing the mean and standard deviation of each replicate measurement sets in all figures.

3.3.1. Effect of acidity

The effect of acidity on the sensitivity, which is a measure of the rate difference between catalytic and noncatalytic reactions, was investigated in the range of 0.1-2.0 mL of 1.5 mol L^{-1} H_2SO_4. The sensitivity, Δ(ΔA), for the fixed-time of first 20 min at 70 °C in Fig. 1 was plotted against the volume of acid by keeping other reagent concentrations constant, and the maximum sensitivity was observed to be 0.5 mL. Sensitivity decreases at lower and higher acid volumes. This high acidity also indicates that the rate of the un-catalyzed reaction is more effective than the catalyzed reaction. At low concentrations, the activation power of Se(IV) may not be effective enough. As a result, 0.5 mL of 1.5 mol L^{-1} H_2SO_4 concentration was considered to be sufficient for further studies.

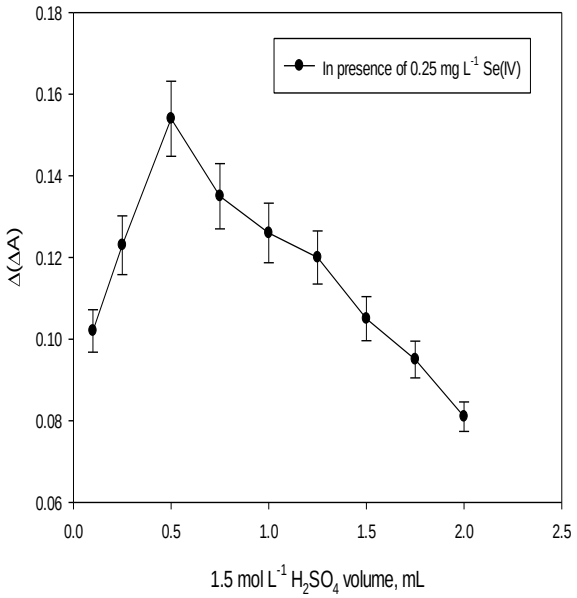

Figure 1. The effect of acidity on sensitivity. Optimal conditions: [Se(IV)]: 250 μg L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0 × 10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5 × 10^{-4} mol L^{-1}, fixed-time: 20 min, temperature: 70 °C at 680 nm.

3.3.2. Effect of reducing agent volume

The effect of the hypophosphite concentration on the sensitivity was investigated using 0.5 mol L^{-1} hypophosphite at constant concentration, by keeping the other reagent concentrations constant at 680 nm in Fig. 2, and its volume was ranged from 0.025 to 1.25 mL for 20 min at 70 °C. The volume of hypophosphite increased for both catalyzed and uncatalyzed reaction in range of 0.025-0.1 mL. At higher volumes, the sensitivity has decreased proportionally as the difference between the rate differences decreases. Therefore, a hypophosphite volume of 0.1 mL was considered as the optimal value.

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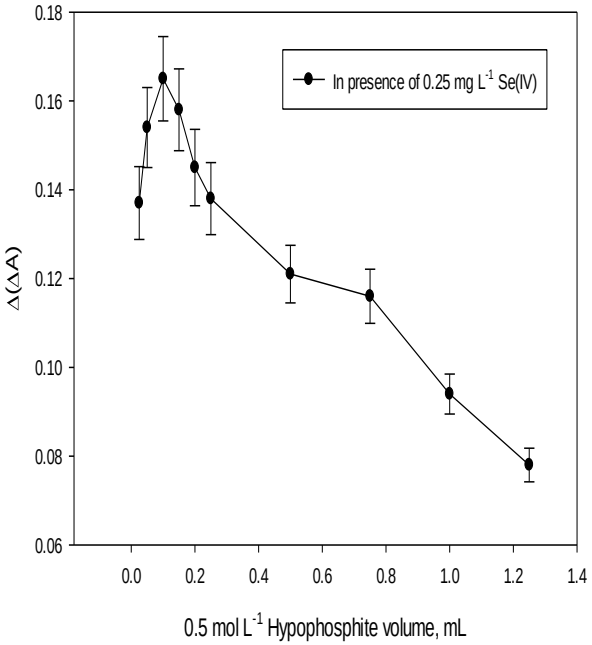

Figure 2. Effect of 0.5 mol L^{-1} hypophosphite volume on sensitivity. Optimal conditions: [Se(IV)]: 250 µg L^{-1}, [PMA]: 0.041 mol L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [Hg^{2+}]: 7.5×10^{-4} mol L^{-1}, fixed-time: 20 min, temperature: 70 °C at 680 nm.

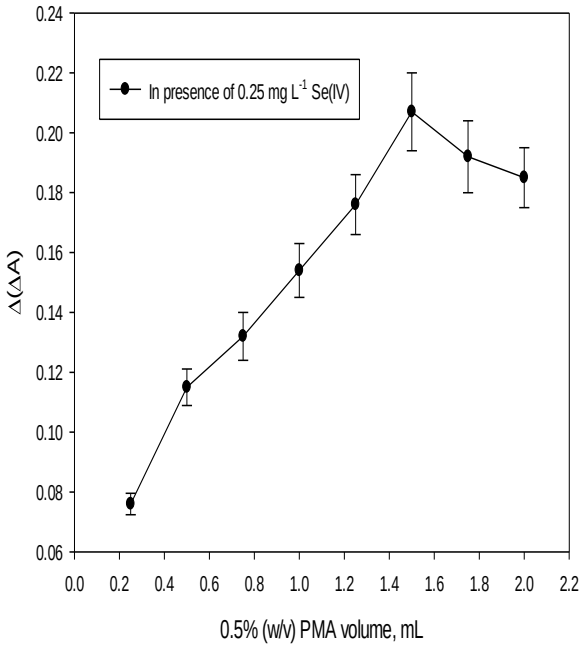

Figure 3. Effect of PMA volume on sensitivity. Optimal conditions: [Se(IV)]: 250 µg L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [$H_2PO_2^-$]: 5.0×10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5×10^{-4} mol L^{-1}, fixed-time: 20 min, temperature: 70 °C at 680 nm.

3.3.3. Effect of PMA volume

The effect of PMA volume on sensitivity was investigated in the range of 0.25-2.0 mL of 0.5% (w/v) in Fig. 3. The sensitivity for the fixed time of 20 min at 70 °C was plotted *versus* its volume, by keeping the other reagent concentrations constant at 680 nm, and the maximum sensitivity was observed to be 1.5 mL. In low volumes, sensitivity has increased up to 1.5 mL, while in higher volumes the slope gradually declines with a decreasing slope. This decrease in sensitivity is due to the fact that the noncatalytic reaction rate is faster than the catalytic reaction. High sensitivity at low volumes can be explained by the fact that the activation power of Se(IV) is more effective. Therefore, a PMA volume of 1.5 mL was considered as optimal for further studies.

3.3.4. Effect of Hg(II) volume

The effect of Hg(II) volume on sensitivity was examined in the range of 0.1-2.0 mL of 0.01 mol L^{-1}. The sensitivity for the fixed time of 20 min at 70 °C was plotted *versus* Hg(II) volume in Fig. 4, by keeping the other reagent concentrations constant at 680 nm, and the maximum sensitivity was observed to be 0.75 mL. Sensitivity increased up to 0.75 mL at low volumes with increasing slope, declined with a decreasing slope in range of 0.75-1.5 mL, and remained constant in range of 1.5-2.0 mL. This decrease in sensitivity may be due to the fact that the non-catalytic reaction rate is faster than the catalytic reaction. Another explanation is that after the Hg(II)-complex formed in the presence of Se(IV) is reduced to Hg(I)-complex by hypophosphite, the reduced complex or Hg_2^{2+} ions can be converted to metallic Hg and Hg(II) by disproportionation. High sensitivity at low concentrations can be explained by the fact that the activation power of Se(IV) is more effective. Therefore, an Hg(II) volume of 0.75 mL was considered as optimal for further studies.

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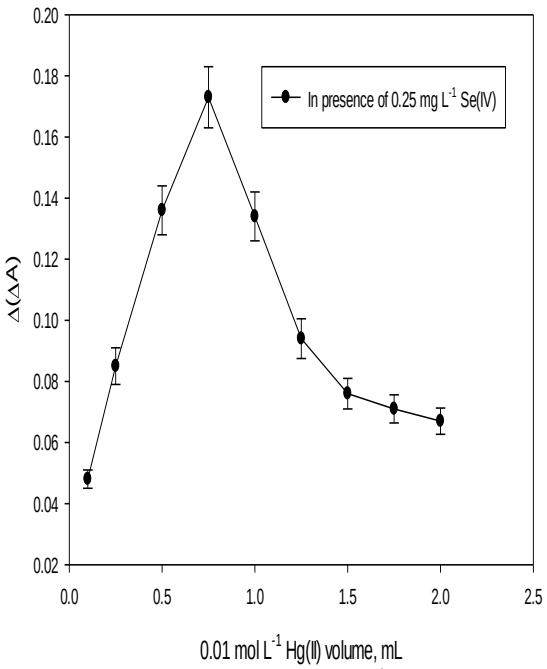

Figure 4. Effect of 0.01 mol L^{-1} Hg(II) volume on sensitivity. Optimal conditions: [Se(IV)]: 250 µg L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0 × 10^{-3} mol L^{-1}, fixed-time: 20 min, temperature: 70 °C at 680 nm.

3.3.5. Effect of temperature on sensitivity

At optimal conditions, the effect of temperature on the sensitivity was investigated in range of 40-85 °C in Fig. 5 because no significant difference in sensitivity was observed in room conditions. Both the catalytic and noncatalytic reaction rates increased with increasing temperature in range of 40-70 °C, in which the rate of catalytic reaction was more pronounced. Sensitivity decreased at temperatures higher than 70 °C. This reduction may be due to the fact that the noncatalytic reaction rate is relatively faster. For this reason, a temperature of 70 °C was considered as optimal for further studies. To check for possible signal fluctuations at this temperature, the analysis was carried out in a water bath, where the temperature was thermostatically controlled with an accuracy of ±0.2 °C.

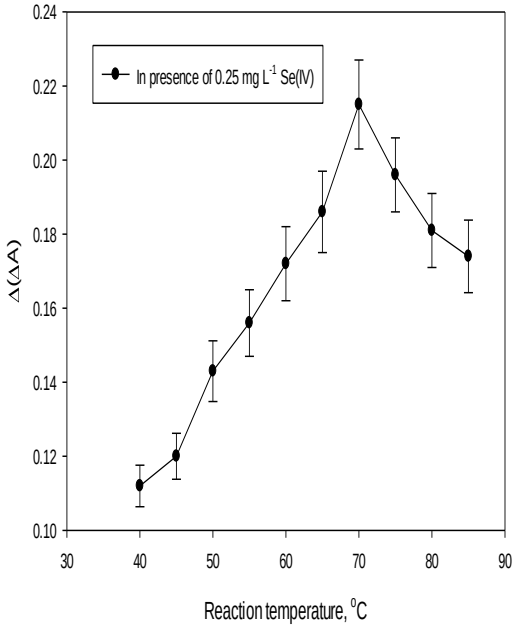

Figure 5. Effect of reaction temperature on sensitivity. Optimal conditions: [Se(IV)]: 250 µg L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0 × 10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5 × 10^{-4} mol L^{-1}, fixed-time: 20 min at 680 nm.

3.3.6. Effect of reaction time on sensitivity

Under optimum reagent conditions, the effect of reaction time on sensitivity was studied in time interval of 5-40 min at 70 °C in Fig. 6. The catalytic and noncatalytic reaction rates were monitored at 680 nm, and the sensitivity increased with increasing time in 5 min intervals; however, the catalytic reaction rate was more pronounced in this time interval. Sensitivity was decreased at longer times than 20 min. This decrease can be caused by acceleration in the noncatalytic reaction rate, so as to lead to a decrease in the signal difference. So, for more advanced applications, a reaction time of 20 min was considered as optimal.

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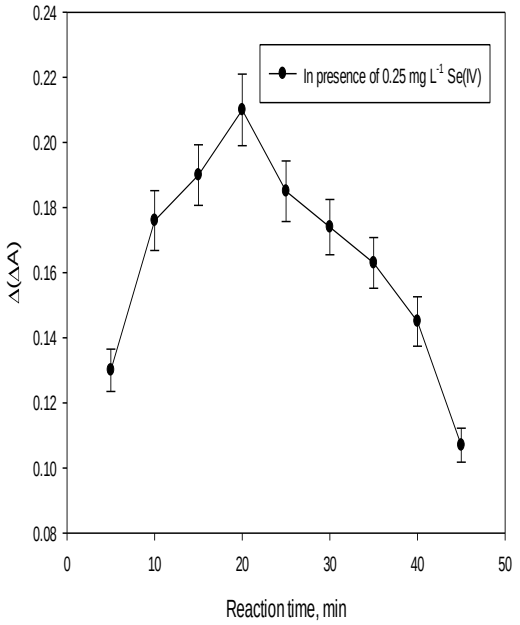

Figure 6. Effect of reaction time on sensitivity. Optimal conditions: [Se(IV)]: 250 μg L^{-1}, [PMA]: 0.041 mol L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [$H_2PO_2^-$]: 5.0×10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5×10^{-4} mol L^{-1}, temperature: 70 °C at 680 nm.

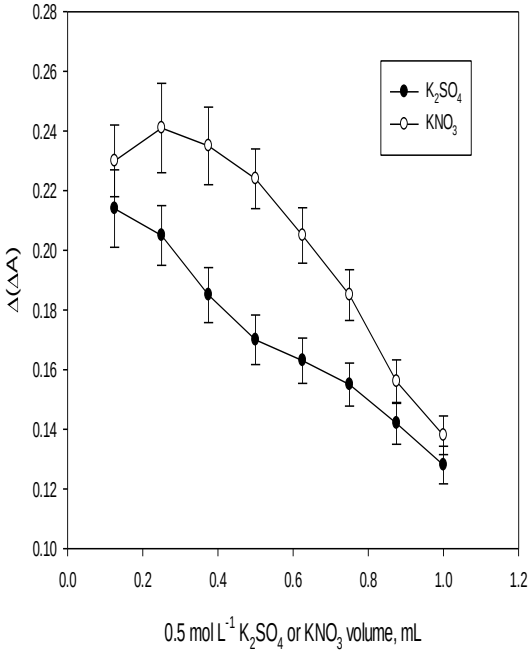

Figure 7. Effect of ionic strength of the medium on sensitivity. Optimal conditions: [Se(IV)]: 250 μg L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0×10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5×10^{-4} mol L^{-1}, fixed-time: 20 min, temperature: 70 °C at 680 nm.

3.3.7. Effect of inert salt concentration as a function of ionic strength on sensitivity

The effect of ionic strength on the catalyzed and uncatalyzed reaction was investigated in the volume range of 0.1-1.0 mL of 0.5 mol L^{-1} KNO_3 and K_2SO_4 solutions in Fig.7. In the presence of KNO_3, at low volumes up to 0.5 mL, the sensitivity did not change, but it began to decline with increasing slope at higher volumes. However, even at low volumes in the presence of K_2SO_4, it was observed that the sensitivity decreased with increasing slope. This indicates that the ionic strength of the environment should be controlled in real complex specimens with high ionic strength. Another solution is to conduct sample analysis with a standard addition calibration curve based on the addition of the known standards of Se(IV).

3.4. Analytical figures of merit

3.4.1. Calibration curve, detection limit, accuracy and precision

Monitoring the net absorbance change according to optimal reagent conditions, different Se(IV) standard calibration solutions for $\Delta(\Delta A) = (\Delta A_C - \Delta A_0)$ were sampled. The results show that the analytical signal against the concentration of Se(IV) in the range of 0.0125-1.0 μg mL^{-1}, $\Delta(\Delta A)$, lies in a sufficiently wide linear range with a regression coefficient of 0.9981 in Fig. 8. In this calibration interval the least squares equation is as follows:

$$\Delta(\Delta A) = (0.80 \pm 0.05) \times C_{Se(IV)}\,[\mu g\ mL^{-1}] + (0.014 \pm 0.001)\ (n: 5, r^2: 0.9981) \quad (4)$$

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v44.4.p57-72

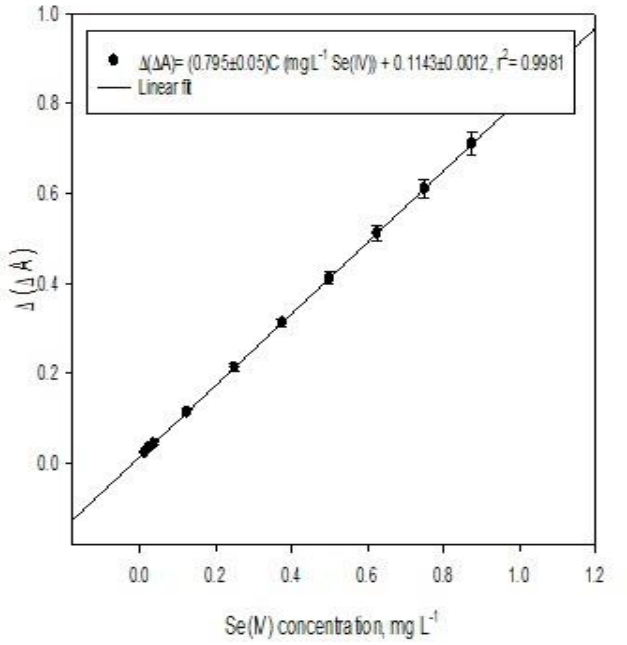

Figure 8. The calibration curve. Optimal conditions: [Se(IV)]: 250 μg L^{-1}, [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0×10^{-3} mol L^{-1}, [Hg^{2+}]: 7.5×10^{-4} mol L^{-1}, 0.5 mL of 0.5 mol L^{-1} KNO_3, fixed time: 20 min, temperature: 70 °C at 680 nm.

The limits of detection and quantification of the present kinetic method (LOD and LOQ) was calculated by taking 3- and 10-folds of the standard deviation of the signal for the ten replicate measurements of the blank solution without analyte, and found to be 3.6 and 12 μg L^{-1}, respectively. Five replicate measurements were performed for different concentrations ranging from 0.0125 to 1.0 μg mL^{-1} and the percent recovery, relative error (RE) and relative standard deviation (RSD) values were found by substituting the analytical signals at the calibration equation. The detailed information is presented in Table 1. From the results, it can be stated that the proposed method is accurate and precise.

Table 1. The accuracy and precision of the five replicate measurement results of Se(IV) at different concentrations. Optimal conditions: [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0×10^{-3} mol L^{-1}, [Hg^{2+}] 7.5×10^{-4} mol L^{-1}, fixed time: 20 min, temperature: 70 °C.

	By fixed time approach of 20 min at 680 nm				
	Added	Found ± SD[a]	Recovery %	RE %[b]	RSD %[c]
Se(IV) (μg L^{-1})	25	24.65 ± 0.80	98.6	-1.40	3.25
	100	99.35 ± 1.48	99.4	-0.65	1.49
	250	251.90 ± 1.76	100.8	0.76	0.70
	750	748.65 ± 2.80	99.8	-0.18	0.37

[a] The average plus standard deviation of five repeated measurements (n: 5).
[b] The percent relative error (RE %).
[c] The percent relative standard deviation (RSD %).

3.4.2. Selectivity

To determine the selectivity of the kinetic method against interferents, the effect of possible interfering species on the rate of catalytic reaction was investigated by changing the concentration of interfering ions to keep the concentration of Se(IV) constant at 250 μg L^{-1} in Table 2. The tolerance limit has been defined as the concentration of interfering species that does not cause more than ± 5.0% of relative error. The results are summarized in detail in Table 2. They indicate that all other interfering species, except for Te(IV), Bi(III), Cu(II) and Sn(IV) ions, do not significantly affect the analytical signal when selenium at the level of 250 μg L^{-1} was determined in a final volume of 10 mL under optimum reagent conditions. The effect of the Te(IV), Cu(II) and Bi(III) ions has been increased to a tolerance ratio ranging from 35 to 70 with addition of thiourea. The interference of Sn(IV) was improved to a tolerance ratio of 50-fold with the addition of NH_4F. Similar errors resulting from positive and negative interactions between analyte and matrix in real samples can be

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v44.4.p57-72

minimized by using the calibration curve approach based on spiking at three concentration levels around quantification limit.

Table 2. The effect of potential interfering species on the determination of 250 μg L^{-1} Se(IV) by the current kinetic method. Optimal conditions: [H_2SO_4]: 0.075 mol L^{-1}, [PMA]: 0.041 mol L^{-1}, [$H_2PO_2^-$]: 5.0 × 10^{-3} mol L^{-1}, [Hg^{2+}] 7.5 × 10^{-4} mol L^{-1}, fixed time: 20 min, temperature: 70 °C.

Interfering species	Tolerance ratio, [$^aC_{iyon}/C_{Se(IV)}$]
NH_4^+, Na(I), K(I), Li(I), Ca(II), Mg(II), Sr(II) and Ba(II)	> 1500
Cr(III), Zn(II), Al(III), $C_2O_4^{2-}$, F^-, thiosemicarbazide, CH_3COO^- and Cl^-	600-1200
Borate, citrate, tartrate, thiourea, SO_4^{2-}, Ni(II), Cd(II), HCO_3^-, ClO_3^- and Ce(III)	350-500
Pb(II), Sn(II), Mn(II), As(III), NO_3^-, HPO_4^{2-} and ClO_4^-	135-300
SCN^-, W(VI), Se(VI), Co(II) and Sb(III)	75-125
SO_3^{2-}, Mn(II), Fe(II), NO_2^-, IO_3^-, Cu(I) and Br^-	35-70
Cr(VI), $S_2O_3^{2-}$, Hg(I), CN^-, I^- and V(IV)	25-35
Fe(III), V(V), Ce(IV), As(V) and Sb(V)	15-25
Te(IV)[b], Bi(III)[c] and Cu(II)[c]	5-10 (35, 50-75)
Sn(IV)[d]	3 (> 50)

[a] C represents the concentration in μg L^{-1}.
[b] The interference of Te(IV) may be greatly suppressed by addition of 1.5 mL of 0.01% (w/v) thiourea solution as a masking agent.
[c] The interference of Cu(II) and Bi(III) ions may be greatly suppressed by addition of 1.2 mL of 0.02% (w/v) thiourea solution as masking agent.
[d] The interference of Sn(IV) may be greatly suppressed by addition of 1.0-2.0 mL 0.025% (w/v) NH_4F as masking agent.

3.4.3. Analytical applications of the method

At initial, the method was applied to samples taken from hot- and cold-spring waters after submitting to certain pretreatments. Samples were treated by using directly kinetic method for analysis of Se(IV). Then, for total selenium analysis, samples were treated by boiling with 4.0-5.0 mol L^{-1} HCl at 85-90 °C for 30 min, for prereduction of Se(VI) to Se(IV). The total Se contents of samples were calculated from the difference between total Se and free Se(IV) amounts obtained by using the kinetic method with and without prereduction. To ensure the accuracy and precision of the method, total selenium levels were also monitored after conversion to hydride with $NaBH_4$ in HCl medium after acidification. From the results obtained by both methods in Table 3, it can be concluded that the current method is as accurate and precision as the routine HG AAS method.

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v44.4.p57-72

Table 3. Determination and speciation analysis of inorganic Se(IV), Se(VI) and total selenium levels in hot- and cold-spring waters by both kinetic method and HG AAS (n: 4).

Samples	By the present kinetic method											By HG AAS			
	Spiking level (μg L^{-1})		[a] Found (μg L^{-1})			[b] Recovery %			[d]RE %		[d]RSD %		[a]Found (μgL^{-1})	[c]Reco-very%	[d]RE %	[d]RSD%
	Se(IV)	Se(VI)	Se(IV)	Se(VI)	Total Se	Se(IV)	Se(VI)	Total Se	Se(IV)	Total Se	Se (IV)	Total Se	Total Se			
Hot-spring water	–	–	5.2 ± 0.3	9.3	14.5 ± 0.5	–	–	–	–	–	5.4	3.6	16.1 ± 0.3	-	-	1.6
	10	100	15.3 ± 0.6	109.5	124.7 ± 0.5	96 ± 3	99 ± 4	99 ± 3	-2.7	-0.6	6.8	8.9	125.7 ± 2.6	99.6	-0.4	2.1
	100	10	105.4 ± 2.9	19.4	125 ± 3	100 ± 1	96 ± 1	99 ± 1	-0.3	-2.2	7.5	7.9	126.3 ± 2.5	100.2	0.2	2.0
	100	100	105.4 ± 2.9	109.5	215 ± 3	99 ± 2	99 ± 4	99 ± 3	-0.6	-1.4	8.4	6.5	215.7 ± 3.6	99.8	-0.2	1.7
Cold-spring water	–	–	4.5 ± 0.1	11.2	15.7 ± 0.1	–	–	–	–	–	4.0	4.7	15.4 ± 0.3	-	-	2.1
	10	100	14.4 ± 0.1	111.3	115.8 ± 0.1	96 ± 3	99 ± 4	99 ±3	-2.7	-0.6	6.8	8.9	125.5 ± 3.2	100.1	0.9	2.6
	100	10	106 ± 0.1	21.3	115.7 ± 0.1	100 ± 1	96 ± 1	99 ± 1	-0.3	-2.2	7.5	7.9	125.8 ± 2.9	99.7	-0.3	2.3
	100	100	114.1 ± 0.1	111.3	215.9 ± 0.1	99 ± 2	99 ± 4	99 ± 3	-0.6	-1.4	8.4	6.5	215.7 ± 3.6	99.8	-0.2	1.7

[a] The average ± standard deviation of replicate measurement results found using both kinetic method and HG AAS.
[b] The spiking recoveries for analysis of Se(IV), Se(VI) and total selenium by the present kinetic method were defined by the following equation: spiking recovery% = C_{found} - C_{real}/C_{added} × 100. Here, C_{found}, C_{real} and C_{added} are the concentration of analyte after the addition of a known amount of standard in the real sample, the concentration of the analyte in the real sample and the concentration of a known amount of standard spiked to the real sample, respectively.

The present kinetic method for validation was applied to two separate SRMs given in Table 4 after sample preparation to analysis with two different wet dissolution approaches and conversion of Se(VI) to Se(IV) by boiling sample solutions at 85-90 °C with 4.0-4.5 mol L^{-1} HCl. To ensure the accuracy of the method, two certified samples were also analyzed by HG AAS, which is an independent comparison method after pre-reduction with $NaBH_4$, by thoroughly dissolving and homogenizing the samples in H_2SO_4 by under ultrasonic effect. The results were quite consistent with the certified values of selenium. The kinetic method after wet digestion with H_2SO_4 appears to be somewhat questionable in terms of both accuracy and precision. This indicates that the selenium present in the sample matrix cannot be fully solubilized and released. It can be said that the result obtained with the other digestion approach is highly compatible with that of the HG AAS, and the results obtained with both methods are quite consistent with the certified values in terms of accuracy and precision. The kinetic procedure was applied to two different SRMs given in Table 4. The results are in good agreement with the selenium values. The relative standard deviations for solid samples were in the range of 5.8-8.7% as a measure of precision. The precision (as RSD%, n: 5) for both SRMs varies between 5.0-6.62%. On the other hand, the precision of HG AAS analysis results was in range of 4.57-5.07%.

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v44.4.p57-72

Table 4. Total selenium levels found in the selected CRMs by the present kinetic method and HG AAS (n: 5)

Samples		By the present kinetic method						By HG AAS			The statistically observed t- and F-values[a]	
		After wet digestion with H_2SO_4			After wet digestion with mixture of HNO_3, H_2SO_4 and H_2O_2			After ultrasonic dissolution in H_2SO_4 medium				
Certified value		Found	RSD %	RE %	Found	RSD %	RE %	Found	RSD %	RE %	t-value	F-value
GBW 07605 Tea	0.072 µg g^{-1}	0.068 ± 0.004 µg g^{-1}	6.6	-5.9	0.070 ± 0.004 µg g^{-1}	5.4	-2.9	0.071 ± 0.004 µg g^{-1}	5.1	-1.4	0.82, 0.30	1.56, 1.11
LGC 6010 Hard drinking water	9.3 µg L^{-1}	9.5 ± 0.5 µg L^{-1}	5.7	+2.1	9.4 ± 0.5 µg L^{-1}	5.0	+1.1	9.4 ±0.4 µg L^{-1}	4.6	+1.1	0.23, 0.25	1.58, 1.19

[a] The statistical t- and F-values observed in the detection of determinate and indeterminate errors for the present kinetic and independent HG-AAS methods for 8 degrees of freedom at 95% confidence level where the critical t- and F-values are 2.31 and 6.39, respectively.

Because of the importance of selenium consumption by foods and beverages such as tea for healthy life, the present method was applied to different brand black and green tea samples after two different digestion approaches. The sensitive and selective method commonly used for total Se analysis such as HG AAS to ensure the accuracy of the method was used in parallel after the ultrasonic-based dissolution approach in H_2SO_4 medium, and the results were found to be highly consistent with those of the present kinetic method. The results were extensively presented in Table 5. A report in literature has shown that the total Se and Se(IV) levels in four commercial tea leaves supplied from different regions of China varied from 191 to 724 µg kg^{-1} and from 173 to 613 µg kg^{-1} respectively[16], which are consistent with our results (ranging from 281 to 708 µg kg^{-1}). Another research group in Turkey has determined a total selenium level of 68 µg kg^{-1} with a standard deviation of 5 µg kg^{-1} in a black tea sample supplied from the market from Turkey[10]. In a similar way, from analysis of the samples by means of ICP OES, it has been observed that total selenium levels are 280/1250 µg kg^{-1} and 1093/1668 µg kg^{-1} respectively in Turkish green and black tea samples with and without lemon. It is clear that lemon addition synergistically increases the selenium concentration in both the black teas and green teas[42]. Selenium is a trace mineral that is essential to good health but required only in small amounts. Selenium is incorporated into proteins to make selenoproteins, which are important antioxidant enzymes. The antioxidant properties of selenoproteins help prevent cellular damage from free radicals. Free radicals are natural by-products of oxygen metabolism that may contribute to the development of chronic diseases such as cancer and heart disease. Other selenoproteins help to regulate thyroid function and play a role in the immune system. In this sense, it can be concluded that citric acid in lemon leads to an improvement in antioxidant property of selenium or selenoprotein in tea.

Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
ISSN: 1678-4618
DOI: 10.26850/1678-4618eqj.v44.4.p57-72

Table 5. Total Se levels found in different tea samples by the present kinetic method and HG AAS (n: 5).

Samples	By the present kinetic method						By HG AAS		
	After wet digestion with H_2SO_4			After wet digestion with mixture of HNO_3, H_2SO_4 and H_2O_2			After ultrasonic dissolution in H_2SO_4 medium		
	Added (μg L^{-1})	[a]Found (μg L^{-1})	[b]Recovery (%)	Added (μg L^{-1})	[a]Found (μg L^{-1})	[b]Recovery (%)	Added (μg L^{-1})	[a]Found (μg L^{-1})	[b]Recovery (%)
Black tea1	–	28 ± 2	–	–	32 ± 2	–	–	31 ± 3	–
	10	38 ± 2	97.0	10	42 ± 2	97.0	10	40 ± 2	97.0
	50	77 ± 5	97.4	50	81 ± 5	98.0	50	81 ± 5	99.8
Black tea2	–	32 ± 3	–	–	34 ± 2	–	–	35 ± 2	–
	10	42 ± 3	98.0	10	44 ± 4	97.0	10	45 ± 3	94.0
	50	82 ± 5	99.6	50	84 ± 5	99.0	50	85 ± 6	99.6
Green tea1	–	63 ± 5	–	–	67 ± 4	–	–	68 ± 4	–
	25	89 ± 6	97.0	25	91 ± 6	97.0	25	93 ± 7	97.0
	50	114 ± 8	98.0	50	117 ± 8	98.0	50	118 ± 8	98.0
Green tea2	–	56 ± 4	–	–	58 ± 4	–	–	58 ± 4	–
	25	90 ± 6	97.0	25	90 ± 6	97.0	25	90 ± 6	97.0
	50	116 ± 9	98.0	50	116 ± 9	98.0	50	116 ± 9	98.0
Green tea3	–	71 ± 6	–	–	72 ± 6	–	–	72 ± 5	–
	25	95 ± 6	97.0	25	98 ± 6	97.0	25	98 ± 6	97.0
	50	128 ± 9	98.0	50	121 ± 8	98.0	50	121 ± 8	98.0

[a] The average ± standard deviation of replicate measurement results found using both kinetic method and HG AAS
[b] The spiking recoveries for analysis of total Se by both the present kinetic method and HG-AAS were defined by the following equation: spiking recovery% = C_{found} - C_{real}/C_{added} × 100 here, C_{found}, C_{real} and C_{added} are the concentration of analyte after the addition of a known amount of standard in the real sample, the concentration of the analyte in the real sample and the concentration of a known amount of standard spiked to the real sample, respectively.

4. Conclusions

A spectrophotometry in visible region with selection of an indicator suitable for analyte is a comparatively low cost, robust and easy-to-operate analytical technique that is readily available in most analytical research laboratories. In the selected kinetic mode, it is a fast, reproducible and versatile technique with analytical frequency of nine samples (three samples plus six calibrations standard) per 20 min. Because the developed method is based on a Se-activated indicator reaction and the final intermediate product is stable for fixed time of 20 min even at a temperature of 70 °C, this detection tool can be efficiently used for the fast, accurate and reliable analysis of selenium species. In addition, the method allows a detection of low levels of Se(IV) up to 3.6 μg L^{-1} in a linear working range of 80-fold without need to a separation/preconcentration step. So, the determination of inorganic selenium species in other sample matrices can be performed even at low concentrations without any matrix effect. Finally, the method can be considered as an alternative to expensive, time-consuming/tedious and complex analytical techniques such as ICP MS, ICP OES, ET AAS or GF AAS, HG AAS, HG AFS, and HG AFS in combination with CE or LC. Moreover, these detection techniques require expert-users in his/her area as well as poor precision and low recovery at low concentrations. Also, the detection limit of the method is especially comparable to most of the similar spectrophotometric and kinetic spectrophotometric methods reported in the literature in terms of linear working range, sensitivity, selectivity and reproducibility. The only disadvantage of the method is that the indicator reaction takes place at high temperature (70 °C) and long time (20 min) limiting sampling rate related to kinetic analysis of samples.

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Eclética Química Journal, vol. 44, n. 4, 2019, 57-72
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