Determination of trace levels of selenium in natural water, agriculture soil and food samples by vortex assisted liquid-liquid microextraction method: Multivariate techniques

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ABSTRACT

A green vortex assisted based liquid-liquid microextraction (VA-LLME) method was developed for preconcentration of selenium. Ammonium pyrrolidine dithiocarbamate (APDC) was used to form a hydrophobic complex with selenium in natural water, agricultural soil and food samples by GFAAS. Whereas Triton X-114, a nonionic surfactant and 1-butyl-3-methylimidazolium hexafluorophosphate ionic liquid were used for Se extraction as a dispersing medium. The conical flasks contents were shack on a vortex mixer to increase the extraction efficiency. Multivariate techniques were used to evaluate extraction parameters; pH, vortex time, APDC amount, volume of ionic liquid and Triton X-114 and centrifugation rate on the recovery of Se. The central composite design (CCD) was used for further optimization of the essential extraction parameters. The enhancement factor and limit of detection were obtained as 98.7 and 0.07 $\mu g\,L^{-1}$. The certified reference materials was used for accuracy of method and the related standard deviation was found to be 3.51%. The resulted data indicated that concentrations of Se in all types of water samples were below the permissible limit recommended by WHO.

1. Introduction

In the periodic table, selenium (Se) is known as one of the important metalloids for the healthy life of animals and humans being. The Se has dual nature, at a lower concentration and it plays an essential micronutrient, while in higher concentrations, it will create toxicity (Nandakumaran et al., 2003; (Hamilton, 2004). The reactivity, toxicity and bioavailability of Se depends on its concentration level in natural water, agricultural soil and food samples. The Se has an important role in immune system functioning, anti-carcinogenic effect and balancing the redox reactions inside the body (El-Bayoumy, 2001). It has a series of critical roles in the biological system, such as enzymatic and structural building systems (Ellis and Salt, 2003). The essentiality and toxicity of Se, especially in humans, depends on its different oxidation states and concentration levels. Selenium induced agricultural soil contamination all over the world and causing a severely harmful effect on the environment. The toxicity of Se is related to lots of diseases, mostly heart and kidney problems (Ji et al., 2012; Lemly, 2004; Sun et al., 2010).

Selenium is considered as a dangerous metalloid; it accumulates in our body, mainly in kidneys which causes mutilation in their process and create severe health hazard (Shaheen et al., 2017). Intake of Se causes calcium regulation and reduces the action of zinc assisted enzymes that can persuade cell injury and death; thus, it is also known as a carcinogenic metalloid (Brozmanová et al., 2010). Generally, environmental pollution by metals/metalloids sources are; fertilizers, pigments, mining and burning of coal, oil and waste materials, building tools, farming and so many others. These processes are the main causes of widespread anthropogenic pollution of water, air and soil across the world (Ali, Kazi et al., 2016a; Ali, Kazi, Baig, Afridi, Arain, Brahman et al., 2015). Selenium deficiency creates oxidative stress that is responsible for producing and developing different types of diseases, namely coronary heart, cancer, diabetes and rheumatism (Ionita et al., 2010; Nogueira and Rocha, 2011).

The highest level of Se concentration was observed in the body organs, such as liver and kidney; meanwhile, it is distributed all over the body system. The concentration of Se in the whole body has been

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reported in the range of 3.0–6.0 mg of those persons who are living in Se deficient area/environments. In comparison, >13.0 mg was found in Se enriched/contaminated regions (Afridi et al., 2015). The liver affects the metabolism mechanism of various metals and metalloids in the body system and accumulates them, to circulate in the blood system. The Se recommended dietary allowance is 55 µg per day for adult's human beings. Biological functioning of Se in animals and human bodies is to synthesize selenocysteine and > 25 selenoproteins (Bruhn et al., 2009). Among them, glutathione peroxides are well known that decreases organic hydro-peroxide and hydrogen peroxide, and at higher levels of glutathione these salts soluble in water or weak acid. In blood plasma, RDA of Se was recently set to maintain the maximum glutathione peroxides activity. The Se is an essential part of some antioxidant enzymes like glutathione peroxides and thioredoxin reductase, which plays catalytic role in some biological reactions and reduces the toxic effect of some elements like arsenic, mercury, etc. (Klapec et al., 2004). The concentration levels of Se in humans being and animals were increased through vegetable, fruit and foods grown in soil enriched with it, in addition to used contaminated fertilizers/biosolids (Afridi et al., 2014; Mattila et al., 2001). Selenium-enriched in agricultural soil can also be a way to decreases the deficiency of Se and get health benefits. Laboratory research indicated that Se in herbs may also play a critical role in therapeutic effects.

As the concentration of Se in natural water is very low, so it is necessary to use different enrichment/preconcentration and separation methods. However some methods were also developed for determination of Se in agricultural soil and food samples, if they contain lower levels of it. Different separation and preconcentration procedures for the determination of Se have been developed such as solid-phase extraction, liquid-liquid extraction, dispersive liquid-liquid microextraction, co-precipitation, cloud point extraction and vortex assisted liquid-liquid microextraction (Ali et al., 2019; Latorre et al., 2013). Previously for the extraction of Se compound by organic solvents which are dangerous, flammable and ecologically harmful (Berijani et al., 2006). Room temperature ionic liquids (RTILs) have been concerned as green solvents used as substitute of conventional volatile organic solvents in different fields of chemistry (Marsh et al., 2002). These are salts liquid over an extensive temperature range together with room temperature. Ionic liquids have some distinctive physicochemical properties such as non-flammability, negligible vapor pressure and better extractability for different hydrophobic complexes of metalloids (Tuzen and Pekiner, 2015).

Multivariate techniques have been more popular nowadays due to its characteristic for optimizing various experimental parameters at a time. The newly developed microextraction method of VA-LLME was optimized by using multivariate techniques, Plackett-Burman Design (PBD) and Central Composite Design (CCD). The both designs have advantages of effective extraction, faster process and lower costs (Panhwar et al., 2014). The PBD was used for screening out the significant extraction parameters in the present VA-LLME method. The PBD was convenient to perform limited numbers of experimental parameters to carrying out newly developed analytical procedure. Therefore, PBD has been employed for optimization of analytical methodology (Bilal et al., 2017; da Luz Lopes et al., 2009).

Different quantification techniques has been applied for the analysis of Se including graphite furnace atomic absorption spectrometry (GF-AAS) (Ghasemi et al., 2010; Qiao-juan, 2010), inductively coupled plasma mass spectrometry and inductively coupled plasma optical emission spectrometry (Habte et al., 2016), The main objective of this research work is to develop a green VA-LLME method for the pre-concentration and extraction of Se in natural water, agricultural soil and food samples. The APDC was used for the formation of a hydrophobic complex with Se and extracted into the fine droplets of ionic liquid (IL). A nonionic surfactant Triton X-114 was mixed into the extraction system as a dispersing medium. At the end, the enriched metalloid complex in IL were back-extracted with aqueous nitric acid (HNO_3) to overcome the matrix effects of IL on determination by GFAAS, as well as enhance the efficiency and selectivity of the proposed VA-LLME method. For complete characterization of VA-LLME methodology, analysis and optimization of the different parameters with multivariate techniques were studied for the enrichment of Se in natural water, digested agricultural soil and food samples.

2. Materials and methods

2.1. Chemicals and glassware

All used reagents are of analytically rank and solutions were made up by reverse osmosis purified water. The chelating agent of APDC was bought from the Fluka Kamica (Bush, Switzerland). Ethanol, Triton X-114 and ionic liquid [C_4MIM] [PF_6] of Sigma-Aldrich (St. Louis, MO, USA) were applied in the proposed VA-LLME method. Triton X-114 (0.1% v/v) solution was prepared by dissolving 0.1 mL in 100 mL of distilled water. Selenium standard solution was prepared by the dilution of stock standard solution of $1000\,mg\,L^{-1}$ (Merck, Darmstadt, Germany). The $0.2\,mol\,L^{-1}$ of HNO_3 was used to make working standards solution. The pH was attuned from 1.0 to 6.0 by drop wise addition of $0.1\,mol\,L^{-1}$ of hydrochloric acid and NaOH in phosphate buffer (monitored with a pH meter). Certified reference material of NCS ZC73032 Celery, soil and sediments (GBW-07309) were obtained from (Gaithersburg, MD, USA).

2.2. Instrumentations

Perkin-Elmer Model, an Analyst 700 (Norwalk, CT) atomic absorption spectrometry attached with graphite furnace (GF-AAS) was applied for the determination of selenium. An operational current of the Se hollow cathode lamp were 7.5 mA with spectral width 0.20 nm, and wavelength 196 nm, all maintained these values during instrumental analysis. A centrifugation with speed ranged from 0 up to 6000 rpm, 220/50 Hz time ranged from 0 to 60 min, (Mechanika Phecyzyjna, Poland), was used for the centrifugation. The pH measurements were performed by using a 720-pH meter, Metrohm.

2.3. Sampling and sample pre-treatment

Different natural water samples such as tap water, drinking water, mineral water, hot spring water (n = 10 of each) have been collected from Tokat City, Turkey. Agricultural soil (n = 10) and food samples (onion, garlic, walnut, hazelnut, chicken meat, canned fish, egg, banana, apple, tomato, potato, spinach, broccoli, cow milk and goat milk) (n = 10 of each) corresponding to total samples (n = 160), were collected from various sampling areas of the agricultural land and local markets in Tokat City, Turkey. All collected food and water samples of different origin were stored in polyethylene plastic bags and bottles, respectively. These samples were transferred as soon as possible into the laboratory and preserved at dry places at 4 °C, till further analysis.

2.4. Microwave digestion procedure

Triplicate of each certified reference material of soil and sediments (GBW-07309), NCS ZC73032 Celery, agricultural soil and all food samples (0.25 g) were taken in digestion Teflon flasks individually. Then mixed freshly prepared 9.0 mL of acid mixture made of HNO_3 (65%) and HCl (37%) in the ratio of 1:3 (V/V) for the digestion of soil samples. Acid mixture contained 6 mL of HNO_3 (65%) and 2 mL H_2O_2 (30%) was used for the digestion of food samples. Microwave digestion conditions for the samples were applied as 2.0 min, about 250 W, 2 min about 0 W, 6 min about 250 W, 5 min about 400 W, 8 min about 550 W, vent: 8 min (Ali, Tuzen, & Kazi, 2016b). After digestion, the samples were diluted to 25 mL for the determination of Se by using ET-AAS technique.

Table 1
Lower and higher values of the extraction parameters used in PBD.

Variables (Abbreviations)	Units	Low	High
pH (pH)	–	1.00	6.00
Vortex mixing time (VMT)	*Sec*	5.00	18.0
Complexing reagent (APDC[a])	mol L^{-1}	0.05	0.25
Volume of Ionic Liquid (IL)	μL	100	400
Surfactant volume (SV)	μL	100	500
Centrifugation rate (CR)	rpm min^{-1}	500	3000

[a] Ammonium pyrrolidine dithiocarbamate.

Table 2
The extraction parameters results used in the PBD (N = 6).

S. NO	pH	VMT (*Sec*)	APDC (mol L^{-1})	IL (μL)	SV (μL)	CR (rpm min^{-1})	Recovery (%)
1	1.0	5.00	0.05	400	500	3000	38.0
2	6.0	18.0	0.05	400	100	500	35.0
3	6.0	18.0	0.25	100	500	3000	56.0
4	1.0	18.0	0.05	100	100	3000	46.0
5	6.0	5.00	0.25	100	100	500	35.0
6	6.0	18.0	0.05	400	500	500	37.0
7	6.0	5.00	0.25	400	100	3000	44.0
8	1.0	5.00	0.25	400	500	500	55.0
9	1.0	18.0	0.25	100	500	500	65.0
10	1.0	18.0	0.25	100	100	3000	80.0
11	6.0	5.00	0.05	400	500	3000	30.0
12	1.0	5.00	0.05	100	100	500	35.0

2.5. Proposed VA-LLME procedure

Triplicate 25 mL of Se standard solution was transferred into tubes (50 mL in capacity). Added 0.05 to 0.25 mol L^{-1} of APDC into the solution of tubes and then adjusted pH in the range of 1.0–6.0 by the addition of NaOH/HCl solution (0.10 mol L^{-1}), in phosphate and acetate buffers. Later on, added 100–400 μL of IL and 100 to 500 μL of 0.01% Triton X-114, then the tubes was capped and vigorously shaken for 5–18 *sec* on a vortex mixer at the speed of 2500 rpm. A cloudy solution was formed, which was then centrifuged for 10 min at 500–3000 rpm to get phase separation. The Se-APDC complex was settled down at the bottom of the centrifuge tube and then removed carefully upper layer of solvent. In the second phase, Se from the viscous IL phase was back-extracted by 0.30 mL of HNO$_3$ (2.0 mol L^{-1}), before analysis by GF-AAS. A blank was also submitted to the same procedure.

2.6. Multivariate techniques

The central composite design (CCD) and placket Barman design (PBD) are useful statistical tests for the optimization and screening out the most significant parameters via using Minitab-16 (Minitab Inc., State College, PA, USA) and Statistica-2007 (Stat Soft, Inc. s, PA, USA) computer program, respectively. These multivariate design are applied to reduce the time for the developed VA-LLME method and provide significant information about the extraction parameters that quickly make data interpretation.

To develop an analytical procedure, VA-LLME using multivariate technique, PBD, to screening out the necessary/unnecessary factors. In present work six factors have been optimized at two levels for which full factorial design have required 64 (2^6) experiments. But these experiments have been decreased to only 12 by the application of PBD. The extraction parameters for developed method, such as pH, vortex mixing time, concentration of the complexing agent, centrifugation rate, volume of IL and Triton X-114 are indicates at its high and low levels in Table 1. The data obtained by PBD are the % recoveries of Se after analyzing six replicate standards of 10 μg L^{-1} of Se. After screening out the extraction parameters which have less effects on the extraction efficiency of analyte were set at one/fixed values for further optimization. The remaining three significant extraction parameters were further optimized by using central 2^{3+} star, orthogonal composite design (CCD) with six degrees of freedom to get the highest percentage recovery of Se by the proposed VA-LLME method. The CCD involving 16 new experiments as shown in Table 2.

3. Results and discussions

3.1. Screening of experimental parameters and their effects

It was observed that the most significant extraction parameters obtained from the resulted data of PBD, corresponding to concentration of APDC, pH and vortex mixing time at a 95% confidence level. The recoveries of the Se due to combined effects from experiment 1 to 12 at higher and lower values of each extraction parameters are shown in Table 2. The highest recovery of Se was observed at higher values of the vortex mixing time, the concentration of APDC and the volume of Triton X-114, as shown in experiment 10 (Table 2). Meanwhile, the lowest recovery of Se was obtained with a combined effect of the lower values of VMT, APDC, volume of IL and centrifugation rate, whereas higher values of pH and Triton X-114 with a recovery of only 30%. The recovery
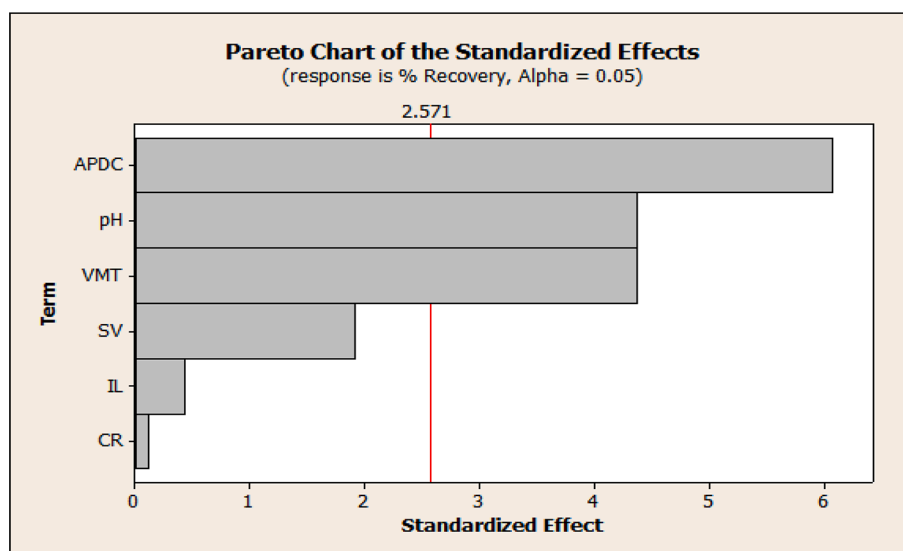

Fig. 1. Pareto chart for the standardized effects of the extraction parameters (APDC, pH, VMT, SV, IL and CR).

Table 3
Significant extraction parameters values in central 2^3 orthogonal composite designs.

| Runs	APDC (mol L^{-1})	pH	VMT (Sec)	Recovery (%)
1	0.15	3.50	11.5	97.8
2	0.05	1.00	5.00	24.0
3	0.25	1.00	5.00	25.0
4	0.05	6.00	5.00	32.0
5	0.25	6.00	5.00	38.0
6	0.05	1.00	18.0	35.0
7	0.25	1.00	18.0	24.0
8	0.05	6.00	18.0	32.0
9	0.25	6.00	18.0	32.0
9	0.02	3.50	11.5	43.0
10	0.32	3.50	11.5	23.0
11	0.15	0.70	11.5	55.0
12	0.15	7.70	11.5	10.0
13	0.15	3.50	0.57	17.0
14	0.15	3.50	22.4	32.0
15	0.32	0.7	11.5	24.0
16	0.15	3.50	11.5	98.0

in experiment 1 with combined effect can be seen at higher values of ionic liquid and centrifugation rate, while at lower values of pH, VMT, APDC concentration and Triton X-114 vol, the recovery was < 40%. The combined effect on recovery of Se indicates in experiment 9 with higher values of vortex mixing time, the concentration of APDC, volume of IL, effect of the lower values of pH, centrifugation rate, and Triton X-114 vol resulted in a recovery of 65%. Whereas in experiment 10, at low values of surfactant, pH and IL, and higher VMT, APDC and centrifugation rate the recovery of Se was found to be 80%. In experiment 3, except IL, all other extraction parameters were at their higher values and the recovery reached 56%. In experiments 2 and 6 at higher values of IL effect shows the decreased recoveries as 35% and 37%, respectively and the remaining extraction parameters values are same as in experiment 3. Therefore, we can see that the volume of ionic liquid has an insignificant effect on the extraction of Se by developed VA-LLME. The maximum recovery of Se was observed in experiments, 3, 4, 9 and 10 at a higher value of vortex mixing time with a combination of other extraction parameters. It showed the major significant effects was vortex mixing

time due to uniformed mixing and extraction of Se in natural water, digested agricultural soil and food samples.

In addition, screening out the effects of each variable on the % recoveries of Se as mention in Table 2, and a Pareto chart for the standardized effects of main factors are also made as shown in Fig. 1. The Pareto chart of the standardized effect can be visualized with alpha value at 0.05 and percentage recovery at 95% confidence interval. It indicates that the factorial design for screening test of the extraction variables was observed at critical value (2.571). It shows that those factors have significant effects, if its experimental value is higher than the critical value.

3.2. Central composite design for optimization of significant parameters

Optimization of the significant extraction parameters was performed by CCD that mostly created by 2nd order response surface modeling (Ali et al., 2019). For further optimization of the advanced VA-LLME method, a central 2^{3+} star orthogonal composite design was also performed employing six degrees of freedom involving 16 runs. Three important extraction parameters, such as APDC concentration, pH and vortex mixing time were considered as significant variables for maximum extraction efficiency of Se in the proposed VA-LLME method. Insignificant extraction variables such as surfactant volume, ionic liquid volume and centrifugation rate were fixed at suitable values as 500 μL, 400 μL and 3000 rpm, respectively (Table 3). Optimum values of all three extraction parameters (APDC, pH and VMT) were obtained as 0.15 mol L^{-1}, 3.5 and 11.5 sec, respectively observed in experiments 1 and 16 with the highest recoveries of Se that was about 98%, as shown in Table 3. Experiment 14 shows the highest value of VMT (22.4 sec), whereas optimum values of the other two factors give the minimum effect on the recovery of Se. The next important variable was pH, which has a crucial role in the formation of the complex for maximum recovery of Se in standards and real samples. The recoveries of Se at the minimum and maximum values of pH in experiments 1 to 8 were observed within 24 to 38%. In experiments 13 and 14, the lowest and highest values of vortex mixing time provided 17 and 32% recoveries of Se, whereas the other two extraction parameters at their optimum values in both experiments. The vortex mixing time is a critical extraction parameter at
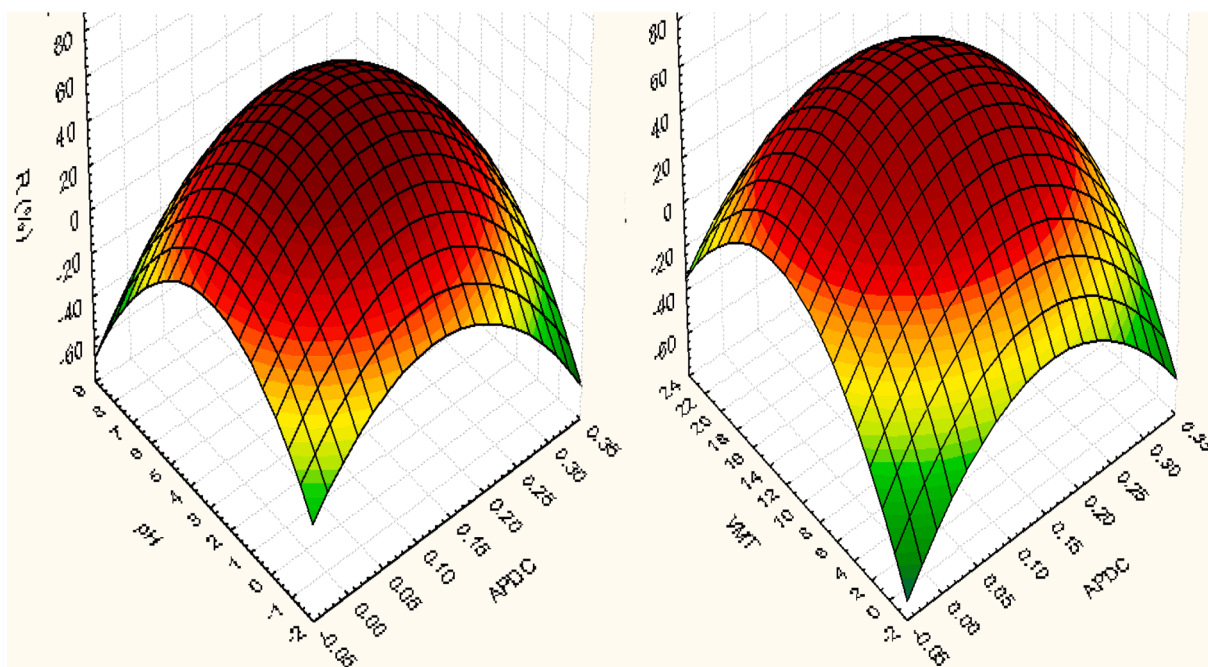
Fig. 2. Central composite design for Se response (a) response between APDC Vs pH and (b) response between APDC Vs VMT.

its lower and higher values, as seen in the proposed VA-LLME method. The interaction between the concentration of APDC vs pH and APDC vs VM time was applied to find out maximum recovery in 3D response surface graphs shown in (Fig. 2a and b). The quadratic equation estimated the anticipated response surface data for maximum recovery in significant extraction parameters. The theoretical optimized values of APDC 0.126 mol L^{-1}, pH 4.71 and VMT 15.3 *sec* were observed for 100% recovery of Se, respectively. Further experiments were performed at optimum values of three significant extraction parameters.

3.3. Effect of interference ions

Effect and interference of the foreign ions on preconcentration and determination of Se were studied in the VA-LLME method. Concerning of the interfering ions in the preconcentration step involves cations that may be less reactive with the selected complexing agent, APDC and decreased extraction efficiency of the Se. For performing out this interference study, 10 mL of a solution containing (1.0 µgL^{-1}) of Se and added different interference ions concentration continuously until the recovery of analyte was affected. The effects of interference ions with their tolerance limits for preconcentration of Se for proposed VA-LLME method. The results shows the tolerance limits of the interfering ions, which give a standard deviation > 5% known as interference ions. The tolerance limit for sodium, potassium, calcium and magnesium was 10,000 mgL^{-1} with recovery > 97.7% due to the formation of an unstable complex of these ions with Se. The recovery of the Se was > 95.1% with increasing concentration of chloride, nitrate, sulfate, phosphate and carbonate up to 5000 mg L^{-1} tolerance limit. The recovery of the Se was > 96.9%, with increasing concentration of aluminum, iron and manganese up to 100 mgL^{-1} tolerance limit. Meanwhile, the tolerance limit for cobalt, nickel, zinc and chromium was up to 50 µgL^{-1} with recovery > 98.4%.

3.4. Analytical figures of merit

The analytical performance of the proposed VA-LLME method was checked after the optimization of the extraction parameters. Linear calibration curve by using Se standards solution was obtained in the range of 0.24–1.75 µg L^{-1} with co-relation coefficient, R^2 = 0.997. The regression equation of the developed VA-LLME method was achieved as $A = 0.29C - 0.05$, where "A" indicated the absorbance and "C" indicated concentration of the standard solutions. The precision of the proposed method was checked by calculating the related standard deviation (RSD %). The RSD % of 3.51 was observed after ten replicate analyses of 1.0 µg L^{-1} Se standard solutions. The limit of detection (LOD) and limit of quantification (LOQ) of the proposed method were calculated by the following formulas:

$$\text{LOD} = \frac{3 \times \delta}{\text{Slope}}, \text{LOQ} = \frac{10 \times \delta}{\text{Slope}}$$

where: Sigma "δ" indicates the standard deviation of 10 new readings and slope from the linear calibration curve after applying the VA-LLME method. The calculated values of LOD and LOQ of the proposed VA-LLME method were found to be 0.07 µg L^{-1} and 0.23 µg L^{-1}, respectively.

The enhancement factor (EF) was observed as a ratio of the slope values from regression equations with and without preconcentration method (Arain et al., 2018). For validation purposes, the developed VA-LLME method was checked by analyzing certified reference material of stream sediments (GBW-07309), NCS ZC73032 Celery. Percentage recovery for analysis of certified reference material (GBW-07309), NCS ZC73032 Celery was calculated by using the following formulas respectively;

$$R(\%) = \frac{\text{Observed concentration}}{\text{Certified cncentration}} \times 100$$

Table 4
Concentration of selenium in certified reference materials using present method.

CRM	Certified value (mg kg^{-1})	Found value (mg kg^{-1})	Recovery (%)
GBW-07309 stream sediment	0.16 ± 0.01[a]	0.158 ± 0.01[a]	98.8
NCS ZC73032 Celery	0.118 ± 0.017[a]	0.116 ± 0.010[a]	98.3

[a] Mean ± standard deviation.

Table 5
Concentration of selenium in agricultural soil, natural water and food samples (n = 10).

Samples	Concentrations
Agricultural soil	1.25 ± 0.06[a] (µg kg^{-1})
Tap water	0.40 ± 0.03 (µg L^{-1})
Drinking water	0.30 ± 0.02 (µg L^{-1})
Mineral water	0.75 ± 0.05 (µg L^{-1})
Hot spring water	0.96 ± 0.08 (µg L^{-1})
Milk samples	Concentrations (µg L^{-1})
Goat milk	89.2 ± 5.31[a]
Cow's milk	54.6 ± 3.50
Food samples	Concentrations (µg kg^{-1})
Onion	72.9 ± 4.81[a]
Garlic	106 ± 9.12
Walnut	35.4 ± 2.19
Hazelnut	41.3 ± 2.60
Chicken meat	81.8 ± 6.28
Canned fish	111 ± 8.43
Egg	137 ± 7.53
Banana	47.1 ± 2.59
Apple	32.7 ± 4.27
Tomato	26.7 ± 1.82
Potato	71.2 ± 4.44
Spinach	105 ± 7.85
Broccoli	66.5 ± 4.16

[a] Mean ± standard deviation.

Finally, the calculated recovery of Se in CRM of stream sediments (GBW-07309) and NCS ZC73032 Celery were > 98.8% as shown in Table 4. The recovery observed for all certified samples are > 98.0%. It indicated that our advanced VA-LLME method is highly validated and accurate for the analysis of natural water, agricultural soil and food samples.

3.5. Application of VA-LLME method

The VA-LLME method was successfully applied for the determination of Se concentrations in different types of water, agricultural soil and food samples. The resulted values of Se 1.25 µg/kg were obtained in agricultural soil from Tokat City, Turkey (Table 5). The Se concentration was found to be low in agricultural soil, different types of water and food samples, which cannot affect human life. The real samples of milk (goat and cow) and food (onion, garlic, walnut, hazelnut, chicken meat, canned fish, egg, banana, apple, tomato, potato, spinach and broccoli) samples were analyzed by using VA-LLME method (Table 5). The population of Tokat city mostly used agricultural products in the form of food and vegetable for energy purposes, depending on the weather. The intake/exposure of Se via drinking waters and eating food including vegetable, by the population of understudy areas possesses less possibility of creating adverse impact due to its lower contents.

The analytical characterization of the proposed VA-LLME method for determination of Se compared with literature reported microextraction methods (Bidari et al., 2008, 2007; Fragueiro et al., 2006; Panhwar et al., 2017; Shrivas and Patel, 2011; Tuzen et al., 2016; Zhang et al., 2013). The analytical characteristics of the developed VA-LLME for determination of Se have observed more advantages as compared to other literature reported microextraction methods. Excellent analytical

Table 6
The comparison of analytical characteristics of the VA-LLME method with reported methods.

Techniques	Methods	LR[j] ($\mu g\,L^{-1}$)	LOD[k] ($\mu g\,L^{-1}$)	RSD[l] (%)	EF[m]	References
GF-AAS[a]	VA-LLME[d]	0.24–1.75	0.07	3.51	98.7	Current Method
GF-AAS	UA-LPME[e]	–	46.1	4.10	50.0	Panhwar et al. (2017)
GF-AAS	SDME[f]	–	0.15	3.00	25.0	Fragueiro et al. (2006)
GF-AAS	DLLME[g]	0.10–3.00	0.05	4.50	70.0	Bidari et al. (2007)
GC-ECD[b]	DLLME	0.015–10.0	0.005	4.10	90.0	Bidari et al. (2008)
ICP-MS[c]	DLLME	0.50–100	0.047	7.20	68.5	Zhang et al. (2013)
GF-AAS	SHT-DSL[h]	0.50–10.0	0.02	4.50	72.0	Tuzen et al. (2016)
GF-AAS	UA-HFLP[i]	0.20–5.00	0.08	3.80	35.0	Shrivas and Patel (2011)

[a] Graphite furnace atomic absorption spectrometry.
[b] Gas chromatography with an electron capture detector.
[c] Inductively coupled plasma mass spectrometry.
[d] Vortex assisted liquid–liquid microextraction.
[e] Ultrasound-assisted hollow fiber liquid phase.
[f] Single drop microextraction.
[g] Dispersive liquid–liquid microextraction.
[h] Switchable hydrophobic-hydrophilic transition dispersive solid–liquid.
[i] Ultrasound-assisted liquid-phase microextraction.
[j] Linear range.
[k] Limit of detection.
[l] Relative standard deviation.
[m] Enhancement factor.

characteristics such as high enhancement factor, low RSD and detection limit as compared to other extraction and preconcentration methods except for some methods shown in Table 6.

4. Conclusion

The proposed VA-LLME method was used for the determination of low-levels of Se concentration in natural water, digested agricultural soil and food samples. The microwave acid digestion method was used for the digestion of agricultural soil and food samples and then applied the developed microextraction method. The advanced VA-LLME method has many advantages such as green, economical, ease procedure, selectivity and sensitivity. Vortex mixer was used for the uniform formation of a complex with APDC and mixing of the dispersive medium Triton X-114 with ionic liquid for Se extraction. It is a green microextraction method by removing toxic organic solvents (acetone, methanol, carbon tetra-chloride and chloroform) by using ionic liquid and Triton X-114 as green alternatives for separation and preconcentration of Se. The interference study shows that it did not interfere with the determination of Se at their respective tolerable limits. The enrichment contents of Se at an ultra-trace level in natural water, agricultural soil and food samples were determined successfully by GF-AAS. The application of factorial design for the screening of extraction parameters shows that concentration of APDC, pH and vortex mixing time is the most significant factor for maximum recovery of Se. The optimum values of all parameters were used for the enrichment of trace level Se in natural water, agricultural soil and food samples.

CRediT authorship contribution statement

Jamshed Ali: Investigation, Validation, Writing - original draft, Writing - review & editing, Software. **Mustafa Tuzen:** Supervision, Investigation, Validation, Writing - original draft, Writing - review & editing, Software. **Xinbin Feng:** Investigation, Validation, Conceptualization. **Tasneem G. Kazi:** Supervision, Investigation, Validation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

Afridi, H. I., Kazi, T. G., Talpur, F. N., Kazi, A., Arain, S. S., Arain, S. A., Brahman, K. D., Panhwar, A. H., Khan, N., Arain, M. S., & Ali, J. (2015). Assessment of selenium and mercury in biological samples of normal and night blindness children of age groups (3–7) and (8–12) years. *Environ Monit Assess, 187*(3). https://doi.org/10.1007/s10661-014-4201-z.

Afridi, H. I., Kazi, T. G., Talpur, F. N., Kazi, A., Arain, S. S., Arain, S. A., Brahman, K. D., Panhwar, A. H., Naeemullah, Shezadi, M., & Ali, J. (2014). Interaction between essential elements selenium and zinc with cadmium and mercury in samples from hypertensive patients. *Biol Trace Elem Res, 160*(2), 185–196.

Ali, J., Kazi, T. G., Afridi, H. I., Baig, J. A., Arain, M. S., Naeemullah, & Farooq, S. (2016a). The evaluation of sequentially extracted mercury fractions in Thar coal samples by using different extraction schemes. *International Journal of Coal Geology, 156*, 50–58.

Ali, J., Kazi, T. G., Baig, J. A., Afridi, H. I., Arain, M. S., Brahman, K. D., Naeemullah, & Panhwar, A. H. (2015). Arsenic in coal of the Thar coalfield, Pakistan, and its behavior during combustion. *Environ Sci Pollut Res, 22*(11), 8559–8566.

Ali, J., Tuzen, M., & Kazi, T. G. (2016b). Determination of Mercury in Environmental Samples by Using Water Exchangeable Liquid-Liquid Microextraction as Green Extraction Method Couple with Cold Vapor Technique. *Water Air Soil Pollut, 227*(6). https://doi.org/10.1007/s11270-016-2863-6.

Ali, J., Tuzen, M., & Kazi, T. G. (2019). Developed of a Green Water Switchable Liquid–Liquid Microextraction Method for Assessment of Selenium in Food and Soft Drink Samples by Using Hydride Generation Atomic Absorption Spectrometry. *Food Anal. Methods, 12*(6), 1298–1307.

Arain, M. S., Kazi, T. G., Afridi, H. I., Bilal, M., Ali, J., & Haseeb, A. (2018). Application of dual cloud point extraction for the enrichment of zinc in serum samples of psychiatric patients prior to analysis by FAAS. *Journal of Industrial and Engineering Chemistry, 62*, 58–63.

Berijani, S., Assadi, Y., Anbia, M., Hosseini, M. R. M.,& Aghaee, E.(2006). Dispersive liquid-liquid microextraction combined with gas chromatography-flame photometric detection: very simple, rapid and sensitive method for the determination of organophosphorus pesticides in water.Journal of Chromatography A, 1123, 1-9.

Bidari, A., Hemmatkhah, P., Jafarvand, S., Milani Hosseini, M. R., & Assadi, Y. (2008). Selenium analysis in water samples by dispersive liquid-liquid microextraction based on piazselenol formation and GC–ECD. *Microchim Acta, 163*(3-4), 243–249.

Bidari, A., Zeini Jahromi, E., Assadi, Y., & Milani Hosseini, M. R. (2007). Monitoring of selenium in water samples using dispersive liquid–liquid microextraction followed by iridium-modified tube graphite furnace atomic absorption spectrometry. *Microchemical Journal, 87*(1), 6–12.

Bilal, M., Kazi, T. G., Afridi, H. I., Ali, J., Baig, J. A., Arain, M. B., & Khan, M. (2017). A new tunable dispersive liquid-liquid micro extraction method developed for the

simultaneous preconcentration of lead and cadmium from lakes water: A multivariate study. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 183*, 417–424.

Brozmanová, J., Mániková, D., Vlčková, V., & Chovanec, M. (2010). Selenium: A double-edged sword for defense and offence in cancer. *Arch Toxicol, 84*(12), 919–938.

Bruhn, R. L., Stamer, W. D., Herrygers, L. A., Levine, J. M., & Noecker, R. J. (2009). Relationship between glaucoma and selenium levels in plasma and aqueous humour. *British Journal of Ophthalmology, 93*(9), 1155–1158.

da Luz Lopes, W., Santelli, R. E., Oliveira, E. P., de Carvalho, M.d. F. B., & Bezerra, M. A. (2009). Application of multivariate techniques in the optimization of a procedure for the determination of bioavailable concentrations of Se and As in estuarine sediments by ICP OES using a concomitant metals analyzer as a hydride generator. *Talanta, 79* (5), 1276–1282.

El-Bayoumy, K. (2001). Overview: The late Larry C. Clark showed the bright side of the moon element (selenium) in a clinical cancer prevention trial. *Nutrition and Cancer, 40*, 4–5.

Ellis, D. R., & Salt, D. E. (2003). Plants, selenium and human health. *Current Opinion in Plant Biology, 6*(3), 273–279.

FRAGUEIRO, S., LAVILLA, I., & BENDICHO, C. (2006). Hydride generation-headspace single-drop microextraction-electrothermal atomic absorption spectrometry method for determination of selenium in waters after photoassisted prereduction. *Talanta, 68* (4), 1096–1101.

Ghasemi, E., Najafi, N. M., Raofie, F., & Ghassempour, A. (2010). Simultaneous speciation and preconcentration of ultra traces of inorganic tellurium and selenium in environmental samples by hollow fiber liquid phase microextraction prior to electrothermal atomic absorption spectroscopy determination. *Journal of Hazardous Materials, 181*(1-3), 491–496.

Habte, G., Hwang, I. M., Kim, J. S., Hong, J. H., Hong, Y. S., Choi, J. Y., Nho, E. Y., Jamila, N., Khan, N., & Kim, K. S. (2016). Elemental profiling and geographical differentiation of Ethiopian coffee samples through inductively coupled plasma-optical emission spectroscopy (ICP-OES), ICP-mass spectrometry (ICP-MS) and direct mercury analyzer (DMA). *Food Chemistry, 212*, 512–520.

Hamilton, S. J. (2004). Review of selenium toxicity in the aquatic food chain. *Science of The Total Environment, 326*(1-3), 1–31.

Herrero Latorre, C., Barciela García, J., García Martín, S., & Peña Crecente, R. M. (2013). Solid phase extraction for the speciation and preconcentration of inorganic selenium in water samples: A review. *Analytica Chimica Acta, 804*, 37–49.

Ionita, L., Bogdan, A. T., Ionita, C., Simion, V., Ivana, S., Ipate, I., … Strateanu, A. G. (2010). Pollution control through ecopathological indicators for nutritional and metabolic disorders by diary cows from farm animals ecosystems near industrially polluted areas.*Advances in Biology. Bioengineering and Environment, 5*, 215–219.

Ji, X., Shen, Q., Liu, F., Ma, J., Xu, G., Wang, Y., & Wu, M. (2012). Antibiotic resistance gene abundances associated with antibiotics and heavy metals in animal manures and agricultural soils adjacent to feedlots in Shanghai; China. *Journal of Hazardous Materials, 235-236*, 178–185.

Klapec, T., Mandić, M. L., Grgić, J., Primorac, L.j., Perl, A., & Krstanović, V. (2004). Selenium in selected foods grown or purchased in eastern Croatia. *Food Chemistry, 85* (3), 445–452.

Lemly, A. D. (2004). Aquatic selenium pollution is a global environmental safety issue. *Ecotoxicology and Environmental Safety, 59*(1), 44–56.

Marsh, K. N., Deev, A., Wu, A.-T., Tran, E., & Klamt, A. (2002). Room temperature ionic liquids as replacements for conventional solvents – A review. *Korean J. Chem. Eng., 19*(3), 357–362.

Mattila, P., Könkö, K., Eurola, M., Pihlava, J.-M., Astola, J., Vahteristo, L., Hietaniemi, V., Kumpulainen, J., Valtonen, M., & Piironen, V. (2001). Contents of Vitamins, Mineral Elements, and Some Phenolic Compounds in Cultivated Mushrooms. *J. Agric. Food Chem., 49*(5), 2343–2348.

Nandakumaran, M., Dashti, H., Al-Saleh, E., & Al-Zaid, N. (2003). Transport kinetics of zinc, copper, selenium, and iron in perfused human placental lobule in vitro. *Molecular and Cellular Biochemistry, 252*, 91–96.

Nogueira, C. W., & Rocha, J. B. T. (2011). Toxicology and pharmacology of selenium: Emphasis on synthetic organoselenium compounds. *Arch Toxicol, 85*(11), 1313–1359.

Panhwar, A. H., Kazi, T. G., Afridi, H. I., Abbasi, A. R., Arain, M. B., Arain, S. A., … Ali, J. (2014). Ultrasonic-assisted ionic liquid-based microextraction for preconcentration and determination of aluminum in drinking water, blood and urine samples of kidney failure patients: A multivariate study. *Analytical Methods, 6*, 8277–8283.

Panhwar, A. H., Tuzen, M., & Kazi, T. G. (2017). Ultrasonic assisted dispersive liquid-liquid microextraction method based on deep eutectic solvent for speciation, preconcentration and determination of selenium species (IV) and (VI) in water and food samples. *Talanta, 175*, 352–358.

Qiao-juan, G. (2010). Determination of trace elements in asparagus (asparagus officinalis l.) by flame atomic absorption spectrometry.*Journal of Anhui. Agricultural Sciences, 8*, 1–10.

Shaheen, S. M., Frohne, T., White, J. R., DeLaune, R. D., & Rinklebe, J. (2017). Redox-induced mobilization of copper, selenium, and zinc in deltaic soils originating from Mississippi (U.S.A.) and Nile (Egypt) River Deltas: A better understanding of biogeochemical processes for safe environmental management. *Journal of Environmental Management, 186*, 131–140.

Shrivas, K., & Patel, D. K. (2011). Ultrasound assisted-hollow fibre liquid-phase microextraction for the determination of selenium in vegetable and fruit samples by using GF-AAS. *Food Chemistry, 124*(4), 1673–1677.

Sun, G.-X., Liu, X., Williams, P. N., & Zhu, Y.-G. (2010). Distribution and Translocation of Selenium from Soil to Grain and Its Speciation in Paddy Rice (Oryza sativa L.). *Environ. Sci. Technol., 44*(17), 6706–6711.

Tuzen, M., Kazi, T. G., & Citak, D. (2016). A new green switchable hydrophobic-hydrophilic transition dispersive solid-liquid microextraction of selenium in water samples. *Analytical Methods, 8*, 2756–2763.

Tuzen, M., & Pekiner, O. Z. (2015). Ultrasound-assisted ionic liquid dispersive liquid–liquid microextraction combined with graphite furnace atomic absorption spectrometric for selenium speciation in foods and beverages. *Food Chemistry, 188*, 619–624.

Zhang, Y., Duan, J., He, M., Chen, B., & Hu, B. (2013). Dispersive liquid liquid microextraction combined with electrothermal vaporization inductively coupled plasma mass spectrometry for the speciation of inorganic selenium in environmental water samples. *Talanta, 115*, 730–736.