Analytical Methods

Green and innovative technique develop for the determination of vanadium in different types of water and food samples by eutectic solvent extraction method

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A B S T R A C T

A green and innovative eutectic solvent based extraction method was proposed for the determination of trace level vanadium in water and food samples by graphite furnace atomic absorption spectrometry. In this extraction technique magnetic stirrer was used for preparation of eutectic solvent by mixing of zinc chloride and acetamide at different molar ratios. Extraction capability of eutectic solvent was increased by adding a non ionic surfactant (Triton X-114) to enhanced phase transfer ratio, to significantly increase the recovery of hydrophobic complex of vanadium with ammonium pyrrolidine dithiocarbamate. A multivariate technique was applied to evaluate the important extraction parameters, which plays important role for optimum recovery of the targeted analyte by proposed extraction method. Multivariate techniques such as (factorial design and central composite design) were applied to screening out the most significant extraction parameters and optimized them. Under optimized extraction conditions, limit of detection and enhancement factor were found to be 0.01 μg L^{-1} and 64.6, respectively. The relative standard deviation for the determination of trace level vanadium at 0.32 μg L^{-1} concentration, was achieved to be < 3.0% (n = 10). Validity and accuracy of the proposed extraction method was checked by analysis of certified reference materials of Canadian lake water and tomato leaves with % age recovery > 98%. The eutectic solvent extraction method was successfully applied for the determination of the trace level vanadium in real water samples of different sources and acid digested food samples, collected from different locations of Tokat city, Turkey.

1. Introduction

The vanadium (V) pollution in environment may creates many health problems in human, animals and plants (Gil et al., 2007; Huang, Huang, Evans, & Glasauer, 2015). Basically V has many oxidation states but most dominant oxidation states are tetravalent vanadium (V^{IV}) and pentavalent vanadium (V^V). The growth of adenosine triphosphate was largely reduced by V^V as compared to V^{IV} in human body (Noblia et al., 2005). Vanadium easily absorbed and accumulated in food, which may creates toxic effect on human, animal and plants (Kachenko & Singh, 2006). Accumulation of V in food and water can reduce growth of plants (Khan, Zaidi, Wani, & Oves, 2009).

The V is naturally present in ores along with other metals. Therefore, volcanic activity is one of the main exposure routes of V to the environment. Uses of V in industries as a stabilizer, anti-corrosive

mediator, color pigment, in nuclear power plants, and manufacture of the nickel-cadmium batteries. Industrial waste material contains high levels of V that can be recycled or dumping and incinerating at agricultural lands which creates pollution (Zeng, Li, & Singh, 2014). It was reported that the emission of V creates worldwide problem (Leblanc et al., 2006). The V can inactivate the antioxidant enzymes, which leads to decreasing their concentration in living cells. Vanadium might be also responsible for the metabolic disorder of essential trace elements (Fraga, 2005). Metabolism of the biological system can be damage due to the excessive intake of V in body, that creates adverse effects on cells (Valko et al., 2007).

Mostly liquid-liquid extraction methods used large amount of organic solvents, which create a rigorous environmental problem (Panhwar et al., 2014; Yousefi & Shemirani, 2010). In modern separation chemistry, it is necessary to reduce use of toxic organic solvents

and reagent that, drastically creates adverse impact on the environment (Ali, Tuzen, & Kazi, 2016). Now a day's low volume of extractant phase is frequently used in liquid-liquid microextraction (Arain, Kazi, Afridi, Ali, & Akhtar, 2017). The expansive application of room temperature IL in many fields, but mostly used for extraction of inorganic pollutants from water samples (Ali et al., 2016; Pena-Pereira, Lavilla, & Bendicho, 2017).

In current literature, the trend of using green solvent for extraction methods has frequently studied. Green solvents must have the following properties like biodegradability, non-toxicity, environmental friendly and recycling ability (Florindo, Romero, Rintoul, Branco, & Marrucho, 2018). In the current method, eutectic solvent (ES) is an emerging green solvent. It also considered as an alternative of ionic liquids. Eutectic solvent is basically composed of many components associated by hydrogen bonding (Wazeer et al., 2018). The melting point of ES have been lower than the individual components, that is < 100 °C (Jenkin et al., 2016). Physicochemical properties of ES almost similar with IL, but ES are much cheaper and environment friendly. Therefore, eutectic solvents have plays an important role in separation sciences (Yang, Cui, & Lv, 2019).

Traditionally, the eutectic solvents (ES) have been prepared from ammonium or/phosphonium based salts and a range of hydrogen bond donors such as organic acid like urea, amide and amines (Abbott, Barron, Ryder, & Wilson, 2007). The ES are economical, have low vapor pressure, environmental friendly and biodegradable (Alonso et al., 2016; Zullaikah, Rachmaniah, Utomo, Niawanti, & Ju, 2018, chap. 2). The ES can be easily prepared from a certain molar ratio of zinc chloride salts and acetamide (as hydrogen-bond donors) by magnetically stirrer bar at 40 °C to form a homogeneous colorless liquid. The synthetic materials used in ES are inexpensive and abundantly available so, it can be applied in large-scale industrial production (Zeng et al., 2014). These ES are generally have high depression and freezing point that is > 150 °C (Van-Osch et al., 2016; Zhang, Vigier, Royer, & Jerome, 2012).

The main objective is to develop a green and innovative ES extraction as an alternative of the classical IL assisted extraction techniques. The ES based green and simple extraction procedure has many advantageous such as inexpensive, biodegradable, non-volatile and non-flammable. Multivariate techniques were used for optimization of the experimental variables which influence the extraction efficiency of V in different types of real water and food samples. Plackett-Burman design was applied to screening out the most effective parameters. While central composite design was used to find out optimum values of variables to obtained maximum recovery of vanadium. In present study evaluate the application of ES for extraction/enrichment of the V in real water samples of different origin and food samples from Tokat City, Turkey.

2. Materials and methods

2.1. Chemical reagents used for preparation of standard solutions

Chemical reagents used in this experiment are of analytical grade. All solutions were prepared by using ultra pure water (Aqua max 18.2 MΩ cm^{-1}, resistivity) obtained from ELGA laboratory (Bucks, UK). 1000 µg L^{-1} of stock standard solution of vanadium was made with salt of NH_4VO_3, obtained from (Merck, Darmstadt, Germany). Series of working standard solutions were prepared freshly by dilution of the stocked standard solution of vanadium. The eutectic solvent was prepared by acetamide and $ZnCl_2$, which were obtained from Sigma (St. Loius, MO, USA). The complexing agent, ammonium pyrrolidine dithiocarbamate (APDC) was purchased from Sigma (St. Loius, MO, USA), and made its 0.1% solution with ethanol and 0.01 mol L^{-1} of acetic acid. The desired pH of the solution was controlled by acetate, phosphate, borate and ammonia buffer solutions (0.1 mol L^{-1}) obtained from (Merck, Darmstadt, Germany). Triton X-114, a non-ionic

surfactant was purchased from Sigma (St. Louis, MO, USA).

2.2. Instrumentations

For the determination of vanadium in real water and food samples by using graphite furnace atomic absorption spectrometer (GF-AAS) obtained from (Perkin Elmer Model 700, Norwalk, CT, USA) was used. Investigation of resulted data was performing by statistical software like Minitab 16 and Statistica computer program 2007 obtained from (Minitab Inc., State College, PA, USA). pH adjustment was performed by a pH meter (Sartorius professional, meter pp-15). The centrifugation was carried out by centrifuge NF-200 modal, obtained from Turkey.

2.3. Procedure of sampling and pretreatment

Fresh water samples of different origin (sea water, waste water, canal water, mineral water, tap water and drinking water) were collected from different sampling location of Turkey. Sea water (10) samples were collected in washed and rinsed polyethylene bottles from Black sea, Turkey. Total 10 samples of each canal and waste water samples were collected in polyethylene bottles from Tokat City, Turkey. River samples (20) were collected in from Yesilirmak River, Tokat, Turkey. Ten samples of each tap and mineral water were collected from Tokat Gaziosmanpasa University. Various agricultural food samples (apple, banana, tomato, spinach and cultivated mushroom) were collected from local market, Tokat, Turkey. All collected fresh and waste water as well as food samples were transferred to analytical laboratory and preserved into the refrigerator at 4.0 °C to avoid loss of analyte and contamination from open atmospheres.

2.4. Procedure of eutectic solvent preparation

Zinc chloride and acetamide (0.125 mol: 0.25 and 0.5 mol) at mol ratio of 1:2 1:4 were used for preparation of eutectic solvent. The molar ratio mixture was taken in a conical flask, placed on hot plate at control temperature (80 °C) and strongly mixed by magnetic stirrer at 500 rpm for 1.0 h until transparent homogenous solution was made, which is called as eutectic solvent for futher analysis. The eutectic solvent at 1:2 M ratio) keep its liquid form, even at lower temperature < 4 °C thus provided a wide range of temperature, however it can be used as a extracting solvent as reported in previous study (Nizamani et al., 2018).

2.5. Procedure of eutectic solvent extraction method

Replicate six samples of real water (25 mL) and different origins and vanadium standard solution containing 1.45–3.40 µg L^{-1} were taken in individual separate polyethylene bottles. Adjusted pH of the solution from 3.0 to 8.0 by using acetate, phosphate, borate and ammonia buffers, then mixing 200–800 µL of 0.1% APDC. Extraction of hydrophobic complex by the addition of eutectic solvent was used in the range of 200–500 µL. Phase separation was enhanced by the addition of 0.1–0.5 mL of Triton X-114 into solution. The contents of tubes were kept at 60 °C temperature on thermostatic bath for 2–12 min. After heating the solutions become turbid, then the solution mixture was transferred into tubes and centrifuged for 10 min at 4000 rpm, to separate aqueous phase and ES enrich hydrophobic complexes of vanadium. The upper layer of analyte rich phase was separated for aqueous layer carefully with the help of micropipette. Then 100 µL of acidic ethanol (0.1 mol L^{-1}, HNO$_3$) was added to ES enriched phase to reduce the viscosity. Finally preconcentrated vanadium solutions of standards/samples were injected into the GF-AAS. Blank solution was also prepared by the same procedure as given above.

2.6. Procedure of multivariate

The main parameters that could affect the extraction efficiency of

vanadium from water and food samples were investigated by perform the preliminary statistical tests. The Plackett-Burman design was performed to screen out the different parameters (n = 5) with 12 experiments instead of 32, which effect the extraction capability of vanadium by eutectic solvent method. For that purposes low and high values of each extracting variables such as pH, volume of complexing agent, volume of eutectic solvent, volume of surfactant and extraction time were selected as 3.0 to 8.0, 100 to 800 μL, 100 to 400 μL, 0.10 to 0.5 μL and 2.0 to 12.0 min, respectively. After screening out the factors that had a less-significant effect on the recovery of the analyte, the other variables were further optimized to provide the maximum recovery of the analyte.

Optimization of the significant parameters observed in PBD design were performed by central 2^{3+} star orthogonal composite design, using Minitab 16 (Inc., State College, PA, USA) and Statistica, 2015. For this design 15 experiments with 6.0 degree of freedom for three significant variables, such as eutectic solvent volume, pH and Triton X-114 concentration were optimized using quadric equation (Table 3). The variables that were not significant as indicated in PBD, including concentration of ligand.

3. Results and discussions

3.1. Analytical performance of parameters

Analytical performance of parameters of the eutectic solvent extraction method was achieved in better way. Linear working calibration curve for V in the range of 0.4–2.48 μg L^{-1} was observed at their optimized value. In this method the regression equation y = 1.292x − 0.017 with a correlation coefficient (R^2) 0.989 was achieved. Limit of detection (LOD) as 3× SD/m and limit of quantification (LOQ) as 10× SD/m, for vanadium in the developed eutectic solvent extraction method was found to be 0.01 μg kg^{-1} and 0.033 μg kg^{-1}, respectively. Where the 'SD' indicated the standard deviation of 10 blank analysis and 'm' indicated the slope of the linear working calibration graph after applying the eutectic solvent extraction method. However the limit of detection (LOD), of samples solution/standards after eutectic solvent assisted enrichment was found to be 0.0085 μg L^{-1}. Enhancement factor (EF) of the developed method was calculated by the slope ratio of calibration graph with and without preconcentration of standards (Zhaolun, Dong, & Xu, 1992). Enhancement factor of the eutectic solvent method was observed 64.6 it shows that our developed method is highly sensitive for determination of ultratrace level vanadium in water and food samples.

3.2. Plackett-burman design for significant parameters

Factorial design and central composite design were performed by using computer based software minitab-16 and Statistica, respectively. The estimated effects of all five variables and percentage recovery of vanadium are shown in Table 1. In proposed eutectic solvent extraction method the Plackett-Burman design was applied to screening out the most significant extraction parameters (Table 1). The standardized Pareto chart of results (Fig. 1), demonstrates the most important effects at 95% confidence intervals, with inference test of the results observed at a minimum t-value is 2.447. Those factors which have t-value, greater than the minimum observed values of 2.447, were considered as significant variables. Among five main parameters, such as eutectic solvent volume (ESV), pH, concentration complexing agent (0.1% APDC), non-ionic surfactant of Triton X-114 (TX-114) and extraction time (ET) were optimized by using % recovery method.

The effects of extraction parameters in the proposed method was observed in the descending order as pH > ESV > Triton X-114 > ligand APDC > ET as shown in Fig. 1. It was observed in experiment 6, the volume of eutectic solvent, pH at (+ve levels), where as concentration of Triton X-114 at (-ve) have significant effect on

Table 1
Significant extraction parameters by Plackett-Burman design.

Experiment	ESV	pH	APDC	TX-114	ET	Recovery (%)
1	+	−	+	−	−	30
2	+	+	−	+	−	46
3	−	+	+	−	+	27
4	+	−	+	+	−	35
5	+	+	−	+	+	48
6	+	+	+	−	+	55
7	−	+	+	+	−	38
8	−	−	+	+	+	27
9	−	−	−	+	+	24
10	+	−	−	−	+	18
11	−	+	−	−	−	20
12	−	−	−	−	−	15

recovery of vanadium in real samples/standards. In experiment 8 and 9 at -ve levels of pH, Eutectic volume, and the % recovery of vanadium was lower.

The pH plays an important role for complex formation with vanadium metal. It forminng selective and stable complex with many metal at their optimized pH values (Naeemullah, Kazi & Tuzen, 2015; Vachirapatama, Dicinoski, Townsend, & Haddad, 2002). Therefore, the complex formation between APDC and vanadium was investigated by optimization of pH in the range from 3.0 to 8.0. It was observed that % recovery of vanadium was low at lower pH values due to competition of hydrogen ion as compared to vanadium reaction with APDC reagent.

In experiments 3, 7, 8, 9, 11 and 12, at low volume eutectic solvent the % recovery of vanadium was found to be lower than those values observed at +levels of ESV. The +ve values of eutectic solvent as extraction medium is due to its capacity to entrapped the vanadium-APDC complex and get higher recoveries. The eutectic solvent volume is a key factor for the extraction efficiency of vanadium by using developed method. Effect of APDC volume on % recovery of vanadium was investigated in the range of 100 μL to 800 μL of 0.1% ligand. It was observed that the recovery of vanadium was not based on the volume of ligands, however it was observed that at (experiment 1 and 2), the volume of ligand are at +v/−v levels, whereas the +ve levels have significant effect. At +ve levels of ligand the % recovery was lower whereas at −ve level, the % recovery was found to be higher (experiment 2). However in case of real matrices the interference of other cautions can be overcome via using optimum amount of complexing reagent.

3.3. Optimization of extraction parameters by central composite design (CCD)

Extraction efficiency of vanadium was check by optimization of five extraction parameter like volume of eutectic solvent, pH, volume of APDC (0.1%) as complexing agent, volume of non-ionic surfactant Triton X-114 and extraction time. It was observed in PBD that volme of ligand and extraction time have less significant effects (p = 0.52–0.845) on the extraction efficiency of V. Therefore the less significant variables (after PBD) were kept at suitable values such as volume of ligand (500 μL) and extraction time (8 min), for central composite design (CCD). The CCD was performed to optimize the three important variable volumes of eutectic solvent, pH and concentration of Triton X-114, using 15 new experiments within six degrees of freedom (Table 2). In experiment 1 and 15, the extraction recoveries of V at optimum values of the eutectic solvent, pH and Triton X-114 were observed 97.2% and 98%, respectively as shown in Table 2. Lower % recoveries were observed at the lowest and highest variable values as indicates in experiments 9, 10, 12 and 13. At lower and higher pH the complex of vanadium is not stable; whereas higher concentration of Triton X114, caused might be enriched analyte have turbid environment.
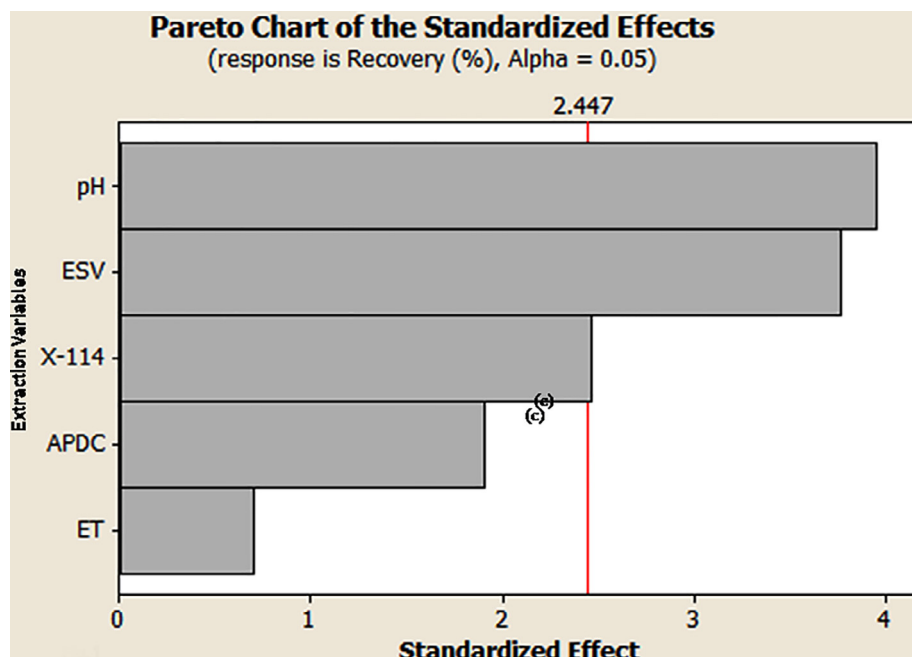
Fig. 1. Pareto chart for the significance of response of the five variables.

Table 2
Central composite design for recovery of the significant extraction parameters.

Experiments	pH	ESV (μL)	TX-114 (mL)	Recovery (%)
1	5.5	350	0.3	97.2
2	8	200	0.1	25
3	3	500	0.1	32
4	8	500	0.1	38
5	3	200	0.5	35
6	8	200	0.5	24
7	3	500	0.5	32
8	8	500	0.5	32
9	1.29	350	0.3	43
10	9.70	350	0.3	23
11	5.5	97.7	0.3	55
12	5.5	302	0.3	10
13	5.5	350	0.3	17
14	5.5	350	0.63	68
15	5.5	350	0.3	98

Table 3
Vanadium concentration in CRMs, agricultural water and food samples.

(a) CRM	Certified value	Obtained value	Recovery (%)
Canadian lake water (TMDA-53.3)	314 ± 15.4 (μg L^{-1})	312 ± 15.7 (μg L^{-1})	98.4 ± 2.3
Tomato leaves (NIST-SRM-1573a)	835 ± 40.7 (μg kg^{-1})	824 ± 42.1 (μg kg^{-1})	98.7 ± 2.6
(b) Agriculture water samples	Added Conc. (μg L^{-1})	Obtained Conc. (μg L^{-1})	Recovery (%)
Sea water	0.0	1.53 ± 0.07	–
	5.0	6.49 ± 0.25	99.2 ± 1.8
Waste water	0.0	1.26 ± 0.08	–
	5.0	6.17 ± 0.35	98.2 ± 2.5
Canal water	0.0	1.05 ± 0.05	–
	5.0	5.93 ± 0.32	97.6 ± 2.8
Mineral water	0.0	1.39 ± 0.13	–
	5.0	6.26 ± 0.52	97.4 ± 3.1
Tap water	0.0	0.72 ± 0.15	–
	5.0	5.53 ± 0.49	96.2 ± 2.4
Drinking water	0.0	0.61 ± 0.18	–
	5.0	5.43 ± 0.51	96.4 ± 2.6
(c) Food samples	Added conc. (μg g^{-1})	Obtained Conc. (μg g^{-1})	Recovery (%)
Apple	0.0	0.55 ± 0.02	–
	5.0	5.41 ± 0.25	97.2 ± 1.7
Banana	0.0	0.13 ± 0.01	–
	5.0	5.09 ± 0.22	99.2 ± 2.1
Tomato	0.0	0.15 ± 0.01	–
	5.0	5.03 ± 0.15	97.6 ± 2.7
Spinach	0.0	0.31 ± 0.04	–
	5.0	5.29 ± 0.21	99.6 ± 1.5
Cultivated mushroom	0.0	0.21 ± 0.03	–
	5.0	5.19 ± 0.19	99.6 ± 1.9

The data obtained by statistical approach CCD among three significant variables for % recovery of vanadium in eutectic solvent extraction method. The 3D response surface plots of each pair of variables between ESV/pH and pH/Triton X-114 shown in Fig. 2 (a, b), respectively. Percentage recovery of analyte after 3D surface response plot was calculated by quadratic equation. The theoretical maximum recovery was observed with eutectic solvent volume (350 μL), pH (5.54) and Triton (0.3 mL), respectively as shown in Fig. 2 (a, b). In the developed eutectic solvent extraction method volume of eutectic solvent have main advantage that greatly affect the % recovery of vanadium from agricultural water and food samples.

3.4. Validation of method

The validity and accuracy of the eutectic solvent extraction method was checked by using certified reference materials of Canadian lake water (TMDA-53.3) and tomato leaves (NIST-SRM-1573a) and spiked the known standard into the real water and acid digested foods solutions. After analysis of CRMs the experimental obtained value of Candian lake water (TMDA-53.3) and tomato leaves (NIST-SRM-1573a) were closed to the certified values of vanadium with % recovery > 98%

(Table 3a). The relative standard deviation for determination of trace level of vanadium at 0.4 μg L^{-1} concentration was achieved to be < 5.0% by 10 replicate analysis. It indicated that our proposed eutectic solvent extraction method was well validated and accurate for analysis of vanadium in real water obtained from different origin and foods samples.
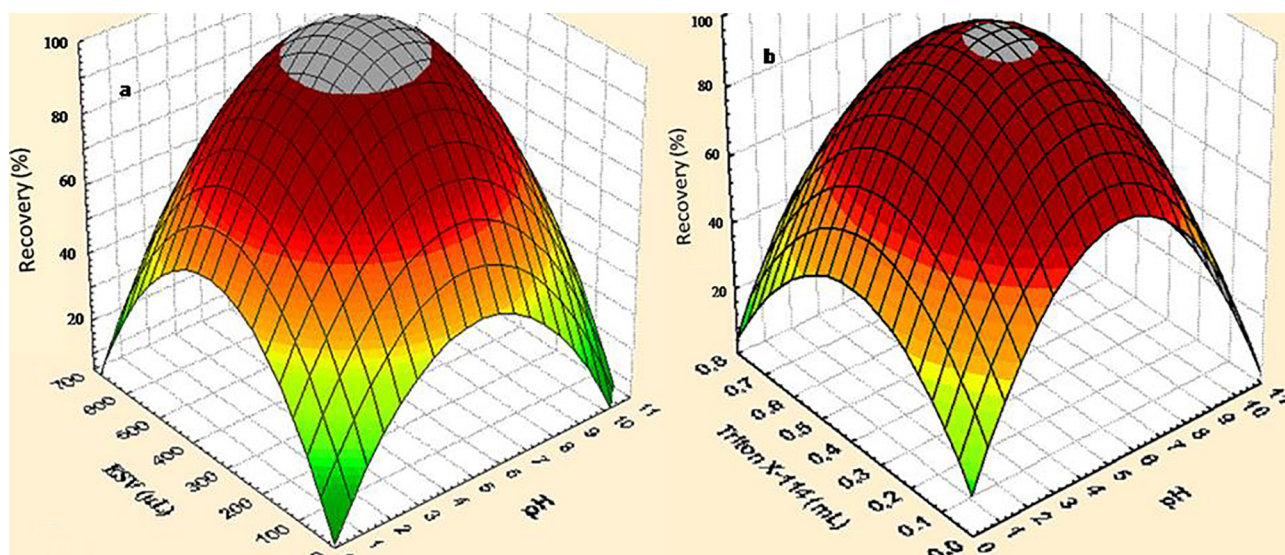
Fig. 2. 3D surface responses for % recovery of vanadium in eutectic solvent extraction method (a) interaction between ESV/pH and (b) interaction between pH/Triton X-114.

Table 4
Comparison of the eutectic solvent extraction with previously reported methods.

Techniques	Methods	LR[a] ($\mu g\,L^{-1}$)	LOD[b] ($\mu g\,kg^{-1}$)	RSD[c] (%)	ET[d] (min)	EF[e]	References
GF-AAS[f]	ESE[j]	0.04–2.48	0.01	2.14	2.1	64.6	This work
GF-AAS	CPE[k]	1.00–60.0	0.05	3.70	5.0	10	(Filik & Aksu, 2012)
GF-AAS	CPE	4.30–130	0.70	4.30	20	10	(Zhu, Zhu, & Wu, 2008)
GF-AAS	SPE[l]	–	100	2.20	30	40	(Ekinci & Koklu, 2000)
GF-AAS	SPE	0.50–10.0	0.04	3.20	15	60	(Lopez-Garcia, Vinas, Romero-Romero, & Hernandez-Cordoba, 2009)
ET-AAS[g]	FI-TILDLME[i]	1.00–15.0	0.48	4.10	15	25	(Berton, Martinis, & Wuilloud, 2010)
ET-AAS	DES-UALPME[m]	0.50–5.00	0.03	3.50	6.0	50	(Zounr, Tuzen, Deligonul, & Khuhawar, 2018)
F-AAS[h]	SPE	0.50–7.00	0.10	2.84	–	55	(Yadamari, Yakkala, & Gurijala, 2014)
UV–Vis[i]	SFODME[n]	3.00–100	0.94	3.90	–	38	(Dadfarnia, Shabani, & Mirshamsi, 2011)

[a] Linear range.
[b] Limit of detection.
[c] Relative standard deviation.
[d] Extraction time.
[e] Enhancement factor.
[f] Graphite furnace atomic absorption spectrometry.
[g] Electrothermal atomic absorption spectrometry.
[h] Flame atomic absorption spectrometry.
[i] Ultraviolet-vissable spectrophotometry.
[j] Eutectic solvent extraction.
[k] Cloud point extraction.
[l] Solid phase extraction.
[m] Deep eutectic solvent bases ultrasonic assisted liquid phase microextraction.
[n] Solidified floating organic drop microextraction.

3.5. Application to water samples

The developed method was successfully used for determination of vanadium in total 60 freshly collected water samples from different locations of Turkey. Ten samples of each, sea water, waste water, canal water, mineral water, tap water were collected and determined vanadium concentration after extraction and preconcentrated by using developed method as given above. Results is in average concentration of vanadium in each individual water samples were found to be low ($< 2\,\mu g\,L^{-1}$) therefore we used standard addition method for accurate determination and reduced the damasking or matrix effects. It was observed that the % recovery after spiking standard concentration > 96% in all studied real water samples as shown in (Table 3b).

3.6. Application to food samples

Microwave method was used for digestion of CRM of tomato leaves and real food samples. For digestion 100 mg of tomato leaves and 1.0 g of apple, banana, tomato, spinach and cultivated mushroom were directly weighed in the polyethylene bottles. Then adding 4.0 mL concentrated HNO_3 and 2.0 mL of hydrogen peroxide (30%) into the polyethylene bottles. Operational condition of microwave digestion method for food samples was applied as reported in our previous work (Ali, Tuzen, & Kazi, 2017). The vanadium level in apple, banana, tomato, spinach and cultivated mushroom are (0.55, 0.13, 0.15, 0.31 and 0.21) $\mu g\,g^{-1}$, respectively (Table 3c). However the resulted data of studied agricultural food samples are very low, therefore we checked their validity by standard addition method in real samples. Percentage recovery after using spiking addition method in each samples were > 97%, which indicate that our developed eutectic solvent extraction

method is excellent for extraction of vanadium at ultra trace level from different food matrixes.

4. Conclusion

The developed eutectic solvent extraction method play an important role for the determination of the trace level V in real water samples and acid digested food samples collected from different sampling locations in Tokat city, Turkey. Optimization of proposed method was performed by a factorial design (Plackett-burman) for screening out the significant parameters, whereas significant variables were further optimized by central composite design. The CCD design was applied for calculation of optimum values of the significant extraction parameter to obtained theoretical optimum value. To calculated and observed optimized values for CRM have good agreement to each other using both instrumental responses and multivariate approach. Concentration of vanadium in real water of different origin and food samples was determined by GF-AAS after preconcentration by applying eutectic solvent procedure. Developed extraction method have many advantages like simple, time consuming, environmental friendly and green for analysis of vanadium in different types of real water and food samples. Analytical figure of merits of the eutectic solvent extraction method indicates low limit of detection, high enhancement factor and excellent % recoveries for CRMs and standard spiking method as compared to literature reported method (Table 4). Therefore, the developed method is highly selective and sensitive for vanadium determination in real water and food samples at ultra trace level concentration with some of complicated matrixes.

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.

Acknowledgments

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