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Scientific paper

Preconcentration and Determination of Trace Vanadium(V) in Beverages by Combination of Ultrasound Assisted-cloud Point Extraction with Spectrophotometry

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Abstract

A novel ultrasound assisted-cloud point extraction method was developed for preconcentration and determination of V(V) in beverage samples. After complexation by pyrogallol in presence of safranin T at pH 6.0, V(V) ions as ternary complex are extracted into the micellar phase of Triton X-114. The complex was monitored at 533 nm by spectrophotometry. The matrix effect on the recovery of V(V) from the spiked samples at 50 μg L^{-1} was evaluated. In optimized conditions, the limits of detection and quantification of the method, respectively, was 0.58 and 1.93 μg L^{-1} in linear range of 2–500 μg L^{-1} with sensitivity enhancement and preconcentration factors of 47.7 and 40 for preconcentration from 15 mL of sample solution. The recoveries from spiked samples were in range of 93.8–103.2% with a relative standard deviation ranging from 2.6% to 4.1% (25, 100 and 250 μg L^{-1}, n: 5). The accuracy was verified by analysis of two certified samples, and the results were in a good agreement with the certified values. The intra-day and inter-day precision were tested by reproducibility (as 3.3–3.4%) and repeatability (as 3.4–4.1%) analysis for five replicate measurements of V(V) in quality control samples spiked with 5, 10 and 15 μg L^{-1}. Trace V(V) contents of the selected beverage samples by the developed method were successfully determined.

Keywords: Ultrasound assisted-cloud point extraction, V(V), Pyrogallol, Safranin T, Beverages, Spectrophotometry

1. Introduction

Vanadium generally exists as two species as V(V) and V(IV), and V(V) is more toxic than V(IV) for living organisms because it can damage the respiratory, nervous and digestive systems.[1,2] While low levels of vanadium are necessary for humans, high concentrations can cause damage by creating a toxic effect. V(V) is also known to be a stronger inhibitor of the enzyme Na- and K-ATPase than V(IV).[3]

Vanadium is more likely to be present in food.[4,5] In fact, it generally exists at levels ranging from 1 to 5 μg kg^{-1} in drinks and fruit juices,[6] from 4 to 41 μg L^{-1} in tea infusions,[7] up to 90 μg L^{-1} in wines[8] and Environmental Protection Agency (EPA) has reported that the allowed limit of vanadium is 50 mg L^{-1}.[9] Because of the low levels of vanadium in foodstuffs, development of simple, easy to use, safe, fast and sensitive analytical methods is of great importance for environmental risk assessment. A number of analytical detection techniques are used for vanadium determination. In general, the most commonly used analytical techniques are flame atomic absorption spectrometry (FAAS),[10,11,12] electrothermal atomic absorption spectrometry (ET-AAS), which is also known as graphite furnace AAS (GF-AAS),[13] inductively coupled plasma mass spectrometry (ICP-MS),[14,15] neutron activation analysis (NAA),[16] inductively coupled plasma-optical emission spectrometry (ICP-OES),[17] fluorometry,[18,19] requiring sample pretreatment steps such as ion-exchange,[20] solid phase extraction (SPE),[21,22] liquid phase microextraction (LPME),[23] and cloud point extraction (CPE).[24–28]

CPE is superior to traditional solvent extraction because of its high extraction yield and preconcentration factor, and has several advantages such as simplicity, inexpensiveness, operational safety and use of non-toxic reagents.[29,30] Before detection, CPE is used as a separation and preconcentration method using a surfactant to cause the generation of micellar surroundings and phase separation when a nonionic surfactant solution (or its mixture with cationic or anionic surfactant) as extractant is heated above the critical temperature. At the determined temperature, the surfactant-rich phase is separated from the diluted aqueous phase by adding a small volume of hydrophobic substance.[31] The CPE process has successfully been used for the separation and preconcentration of trace levels of V(V) or V(IV) from different sample matrices[6,29,32–36] using different chelating agents. In this sense, there are some publications dealing with CPE-spectrophotometric determination of vanadium in different sample matrices with their own advantages and disadvantages.[24–28] Moreover, solidified floating organic drop microextraction (SFODME)[37] and on-line temperature-assisted ionic liquid based dispersive liquid liquid microextraction (on line TA-IL-DLLME)[38] in combination with spectrophotometry as further preconcentration tools prior to analysis were also used for sensitive determination of vanadium in environmental samples.

The objective of the present study is to develop a simple, sensitive and selective ultrasound assisted-CPE (UA-CPE) method coupled to spectrophotometry for determining vanadium levels present in beverages. Ultrasound energy was used to increase the extraction rate at micellar interface and to improve the extraction efficiency. The proposed method is based on the complexation reaction of V(V) by pyrogallol in the presence of cationic phenazine group dye, safranin T as ion-pairing agent at pH 6.0, and extraction of the formed ternary complex into the micellar rich phase of Triton X-114. In order to attain high recovery, selectivity, and precision for the determination of V(V) in beverage matrices by spectrophotometry after preconcentration by UA-CPE, the various analytical parameters affecting the complex formation and the extraction efficiency with minor sample treatment were investigated and optimized. The UA-CPE procedure can be an alternative to other separation/preconcentration procedures for the trace analysis of vanadium in other sample matrices of nutritional and toxicological importance like foodstuffs.

2. Experimental

2. 1. Instrumentation

The absorbance measurements were performed using a double-beam UV-Visible Spectrophotometer (Shimadzu UV-1800 PC, Kyoto, Japan) equipped with the 1.0-cm quartz cells. The pH measurements were made using Jenway 3010 pH meter (Staffordshire, UK). A centrifuge apparatus (Hettich Universal, Universal-320, Hettich Centrifuges, UK) was used for the phase-separation procedure. An ultrasonic bath operating with a frequency of 40 kHz at power of 300 Watt (UCS-10 model, Seoul, Korea) was used efficiently to control and to keep constant the determined temperature for the UA-CPE.

2. 2. Reagents and Solutions

The analytically pure reagents were used, and all solutions were prepared from doubly distilled water during the analysis. Stock solution of V(V) (1000 mg L^{-1}) was prepared from ammonium metavanadate. All standard solutions were prepared daily. A 0.1 mmol L^{-1} safranin T and 0.081 mmol L^{-1} pyrogallol solution were prepared from standard solutions. To protect its stability against oxidation, it was prepared by dissolving in methanol containing 1.0 mol L^{-1} HCl and diluting with water, and kept in dark. The solutions (1.0%, *w/v*) of Triton X-114 and Triton X-45 (Sigma) as extractants were prepared by thoroughly mixing with vortex in 100 mL of water, and were used without further purification. The electrolyte solutions of 0.01 mol L^{-1} were prepared by using suitable amounts of KCl and KNO_3 in deionized water. The universal Britton-Robinson buffer solutions at pHs ranging from 3.0 to 8.0 were prepared by mixing H_3BO_3, H_3PO_4 and CH_3COOH at equal molar concentrations (0.04 mol L^{-1}) with 0.2 mol L^{-1} NaOH and adjusting to a suitable pH value by a pH meter.

2. 3. Procedure for UA-CPE

In the UA-CPE, an adequate amount (approx. 3.0 mL) of sample solution or a standard V(V) solution in a linear range of 2–500 μg L^{-1}, 1.6 mmol L^{-1} of B-R buffer solution at pH 6.0, 1.6 μmol L^{-1} of pyrogallol, 2.0 μmol L^{-1} of safranin T, 6.0 mmol L^{-1} of KCl solution, and 0.05% (*w/v*) Triton X-114, respectively, were sequentially transferred to a conical tube. Then, the solution was diluted to 50 mL with water. Afterwards, the resultant solution was placed in an ultrasonic bath (300 W, 40 kHz) and sonicated at 50 °C for 3 min. The final solution was centrifuged at 4000 rpm for 15 min for separation of the aqueous and surfactant-rich phases. After centrifugation it was cooled down in an ice bath for 10 min to facilitate phase separation. After cooling in an ice bath, the supernatant aqueous phase was separated from the aqueous bulk phase. The surfactant rich phase in the tube was diluted by adding 1.5 mL of ethanol to reduce its viscosity. The above mentioned procedures were also repeated for blank solution. At last, the total V contents as V(V) of all the pretreated and extracted samples and SRMs were spectrophotometrically monitored at 533 nm.

2. 4. Sample Preparation

All beverage samples used in this study were purchased from a supermarket in Sivas, Turkey. Firstly, 25 mL of beverage samples were pretreated by trichloroacetic acid (3.0% (*w/v*), 5 mL) for destruction of organic matrix due to being rich in protein and fat. Subsequently, the mixture was mixed with vortex, precipitated at 4000 rpm for 15 min and filtered by the membrane filter. Before analysis, in order to test the accuracy and precision of the proposed method, all samples including the pretreated milk samples were subjected to two digestion process in parallel, until obtaining completely clear, colorless, homogenous digests.

The steps of the experimental procedure: 20 mL of beverage samples in plastic type boxes, 6 mL of 65% (*w/w*) HNO_3 and 4 mL of 30% (*w/w*) H_2O_2 (3:2, *v/v*) were transferred in a 100 mL conical flask. The obtained mixture was heated at 120 °C nearly to dryness. The mixture was diluted to 50 mL with water after cooling to room temperature and centrifuged. The pH of the mixtures was adjusted to the desired values (7.0) using 0.1 mol L^{-1} NaOH solution. The process was then repeated to determine total V levels as a measure of V(V) concentration by taking approximately 3 mL of the beverage samples at the optimal conditions.

The steps of the second sample digestion treatment using ultrasound: 20 mL of the samples, a mixture of 4 mol L^{-1} HNO_3, 4 mol L^{-1} HCl and 0.5 mol L^{-1} H_2O_2 (1:1:1, *v/v*) were sequentially transferred to the 100 mL conical flask. Then, the resultant solution was diluted to 100 mL with water and kept in the ultrasonic bath for 20 min at 60 °C (300 W, 40 kHz). The phases were separated by centrifugation for 15 min at 4000 rpm. The separated solution was completed to 50 mL with water, and its pH was adjusted to 7.0 by NaOH solution. The process was applied to determine total V levels as a measure of V(V) amount by taking approximately 3 mL of the sample under the optimal conditions.

3. Results and Discussion

In order to determine the optimum conditions, the analytical variables involved in complex formation such as pH, buffer concentration, concentrations of pyrogallol as chelating agent, safranin T as ion pairing reagent and surfactants, including operational factors affecting extraction efficiency such as centrifugation rate and time, temperature and time for the determination of V(V) at 50 μg L^{-1} were investigated in detail.

3. 1. Effect of pH

CPE procedures used in the separation and extraction of metal ions need the formation of a hydrophobic metal-chelate complex to be extracted in the surfactant-rich phase. The pH plays a significant role in metal-chelate complex formation. It affects the charge of the analyte, therefore it affects the generation of the extractable hydrophobic complex between the metal and primary/secondary ligands with the hydrophilic and hydrophobic centers of surfactant.[39] Thus, extraction efficiency is highly dependent on the pH at which complex formation is investigated. A set of similar experiments were carried out in the pH range of 3.0–8.0 in Britton Robinson buffer. The effects of pH on the extraction of V(V) complex are given in Figure 1(a). In the pH range of 5.5–6.0, extraction was quantitative. When the pH values are below or above 6.0, extraction efficiency decreases due to uncomplete complex formation and probable degradation of the complex (for fast oxidation of $VO(OH)^+$ species with dissolved oxygen) at increased pHs, respectively.[33] The V(V) ion is often present in forms of VO_2^+ (pH < 3.5), $H_2VO_4^-$ or $VO_2(OH)_2^-$ (pH 3.5–7.5) and HVO_4^{2-} or $VO_3(OH)^{2-}$ (pH 7.513.0).[40,41] However, V(IV) starts to hydrolyze and dimerize at pH 4.0; the pK_a value of the $[VO(H_2O)_5]^{2+}$ ion has been noticed to be in the range 5.3–6.0. At pH 5.0, insoluble $VO(OH)_2$ starts to form, which turns into water-soluble $[(VO)_2(OH)_5]^-$ and $[VO(OH)_3]^-$ complexes in strongly alkaline aqueous solution. As a result of reduction of V(V) to V(IV) in the presence of a reducing, chelating agent such as pyrogallol (HL) and redox sensitive ion-pairing reagent, safranin T, it can be expected that V(IV), proportional to V(V) concentration, forms a pH dependent anionic chelate complex in presence of safranin T as follows:

$$VO_2(OH)_2^- + 2HL \rightarrow VO_2L_2\text{-} + 2H_2O \qquad (1)$$

$$VO_2L_2^- + 2H^+ + e^- \rightarrow VOL_2 + H_2O \qquad (2)$$

$$VOL_2 + SF^+ + H_2O \rightarrow [VO(OH)L_2\text{-}\ldots SF^+], \text{ ion-association complex} + H^+ \qquad (3)$$

Therefore, pH 6.0 was selected as the optimal value. When considering complex formation with V(V) or V(IV), it is implied that V(V) can be reduced to V(IV) easily owing to the sufficient redox potential ($VO_2{}^+/VO^{2+}$: 1.00 V in a strongly acidic solution) given in the literature.[42] Also, it was assumed that V(V) was reduced to V(IV), and this fact was confirmed by ESR analysis of vanadium adsorption on a persimmon tannin gel from the NH_4VO_3 solution at pH 6.0, due to the formation of a stable complex of V(IV) with catechol and pyrogallol groups in the gel. With a complex formation constant of pK_f: 16.67, this state is attributed to the fact that vanadyl cation,VO^{2+}, a strong acid, forms stable complexes with both strong bases, catechol and pyrogallol, as a result of the tannin gel adsorbs VO^{2+} ions with high efficiency.[43] In a similar way, it was confirmed that in the interaction with 2,6-dithiolphenol at pH 4.0, V(V) initially reduced to V(IV), and the produced V(IV) gave anionic chelate complex, VOL_2^{2-}, and then formed ion-pairing complexes with hydrophobic amines , *o*-, *m*- and *p*-toluidine derivatives (as R-NH_3^+) detected by both spectrophotometry and ESR spectrometry.[44] Moreover, so as to support the mechanism of complex formation, from potentiometric titration data obtained in two separate studies,[45,46] including other studies based on ion-association,[47,48] it has been observed that pK_a value of chelate complex formed between vanadyl ion, VO^{2+} and pyrogallol at pHs near to neutral is 5.40 where it spontaneously forms a highly stable complex with a logK_f ranging from 22.97 to 21.68 at pHs near to neutral, gradually decreasing with increasing temperature in range of 25–45 °C. Also, under optimal conditions, it has been observed that after pre-reduction and hydrolysis in absence and presence of safranin T as ion pair, vanadium is complexed with pyrogallol in form of anionic $VO(OH)L_2^-$ with a logK_f of 20.9 with relative error of –3.6% at pH 6.0, and then extracted as the hydrophobic ternary complex in form of $VO(OH)L_2SF$ into the micellar phase with stoichiometric ratios 1:2 and 1:2:1, as determined using the molar ratio and Job's continuous variation methods. In light of all these findings, the influence of buffer concentration in range of 0.15–2.0 mmol L^{-1} at pH 6.0 in Figure 1(b) was also investigated, and the maximal and stable signal was provided at a buffer concentration of 1.6 mmol L^{-1}.

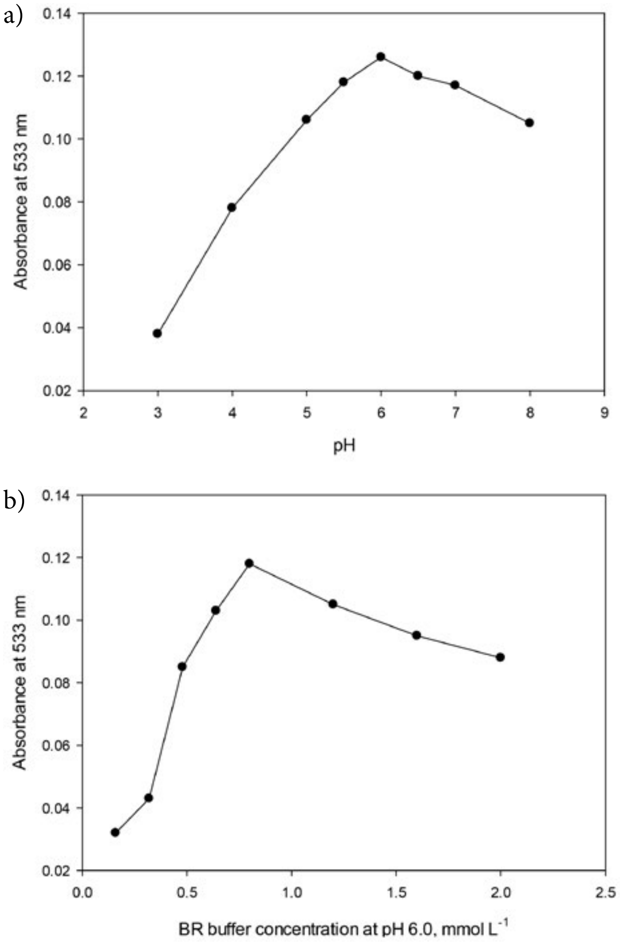

Figure 1. The influence of (a) pH and (b) B-R buffer concentration at pH 6.0 on the analytical signal. Conditions: 50 μg L^{-1} V(V), 1.6 μmol L^{-1} pyrogallol, 2.0 μmol L^{-1} safranin T, 6.0 mmol L^{-1} KCl solution, and 0.05% (*w/v*) Triton X-114 at 50 °C and incubation for 3 min.

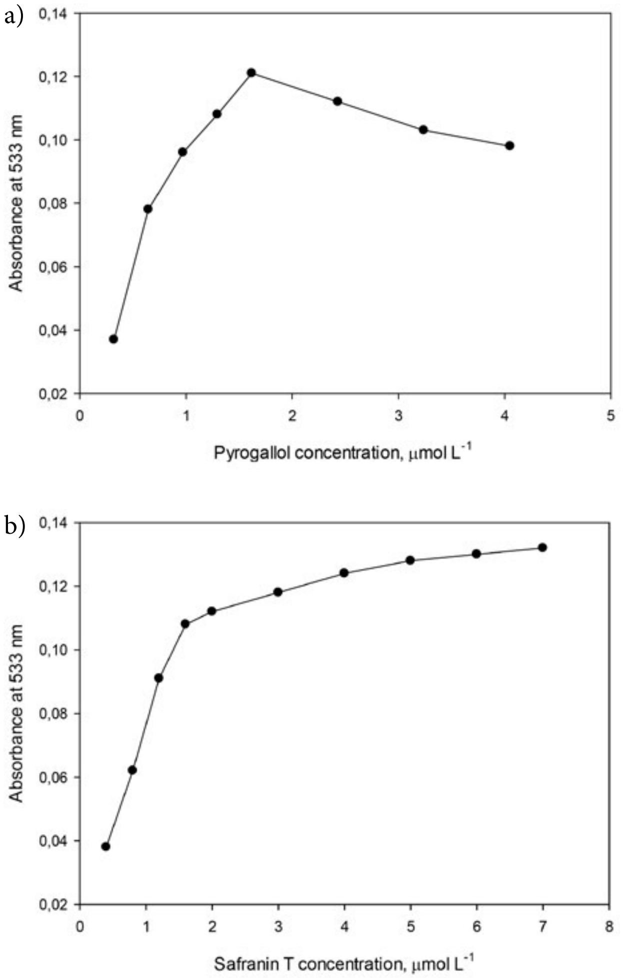

Figure 2. The influence of (a) pyrogallol concentration and (b) safranin T concentration at pH 6.0 on the analytical signal. Conditions: 50 μg L^{-1} V(V), 0.8 mmol L^{-1} B-R buffer at pH 6.0, 6.0 mmol L^{-1} KCl solution, and 0.05% (*w/v*) Triton X-114 at 50 °C and incubation for 3 min.

3. 2. Effect of Pyrogallol and Safranin T Concentrations

At the optimal pH, the influence of the pyrogallol amount as the main chelating agent in the range of 0.3–4 μmol L^{-1} was studied, and the results are demonstrated in Figure 2(a). It can be seen that the analytical signal value for V(V) initially increases with increasing slope and reaches the maximum value while pyrogallol concentration linearly increases up to a concentration of 1.6 μmol L^{-1}. At higher concentrations than 1.6 μmol L^{-1}, the analytical signal gradually decreases, due to the charge transfer complex formation between pyrogallol and safranin T in absence of V(V) by donor-acceptor mechanism.[49] Therefore, pyrogallol concentration of 1.6 μmol L^{-1} was chosen as the optimal concentration for the subsequent experiments.

The influence of safranin T amount as ion-pairing reagent on the extraction yield of V(V) was studied in the range of 0.4–7 μmol L^{-1}; the obtained results are represented in Figure 2(b). The absorbance value increased with increasing ion-pairing concentration for V(V), so as to show a linear relationship with two different slopes. However, the absorbance sharply increases with a sensitivity increase of 9-fold in low concentration region of 0.4–2 μmol L^{-1}. After the concentration of 2 μmol L^{-1}, in a similar way, the absorbance shows a linear increase in range of 2–7 μmol

L^{-1}, but this increase in signal slows down with a lower slope, so as thermodynamically to reach a plateau at a saturation point. Perhaps, the aggregation of safranin T at higher concentrations may cause a decrease in the absorbance value. The literature findings show that safranin T, which is a redox-sensitive dye, has a dimerization constant of K_D: 4.73 at high concentrations.[50] Thus, 2 μmol L^{-1} of safranin T was determined as the optimal value for further studies.

3. 3. Effect of Triton X-114 Concentration

The nonionic surfactant concentration as extractant is one of the most important factors affecting the CPE of metal ions. Usually, non-ionic surfactants such as Triton X-114, Triton X-45, PONPE 7.5 were extensively used in CPE of V(V). The non-ionic surfactants are used to create micelle aggregates, these very efficiently capture the complexes, so as to get simple phase separation. The surfactants have relatively low cloud point temperature, high extraction yield, are commercially available, of high purity, nonvolatile and of low toxicity.[51,52] However, surfactant concentrations in range of 0.006–0.06% (*w/w*) were used. Figure 3(a) shows the effect of non-ionic surfactant concentration, the maximal extraction efficiency and higher signal was obtained by using 0.05% (*w/w*) Triton X-114 while a concentration of 0.06% (*w/w*) for Triton X-45 was needed. Thus, Triton X-114 with a significant sensitivity difference was chosen as adequate non-ionic surfactant. Its concentration of 0.05% (*w/v*) was fixed for subsequent studies. At values above this concentration, the extraction efficiency was slightly lower due to the increase in the volume and the viscosity of the surfactant-rich phase.[53] Below this value, the decrease in the absorbance as a measure of extraction efficiency is due to deficiency of the surfactant assemblies to extract the hydrophobic complex quantitatively.[54]

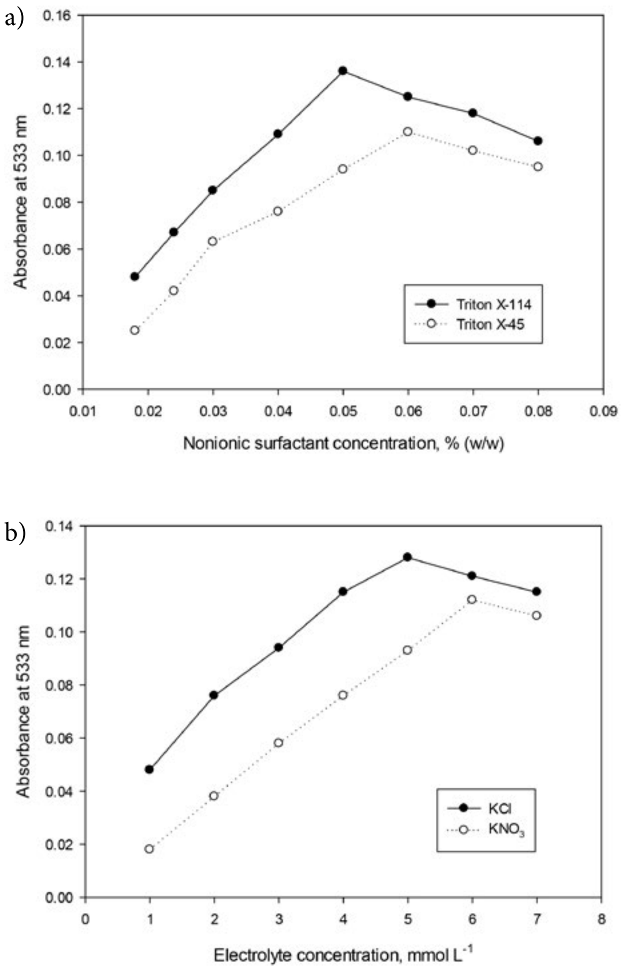

Figure 3. The influence of (a) nonionic surfactant concentration and (b) electrolyte concentration at pH 6.0 on the analytical signal. Conditions: 50 μg L^{-1} V(V), 0.8 mmol L^{-1} B-R buffer at pH 6.0, 1.6 μmol L^{-1} pyrogallol, 2.0 μmol L^{-1} safranin T at 50 °C and incubation for 3 min.

3. 4. Effect of Ionic Strength

The ionic strength of the solution can influence the extraction process and yield of extraction owing to altered density of the aqueous phase and remarkably simplify phase separation. Therefore, the effect of ionic strength on the CPE was also studied by observing the extraction efficiency for several electrolyte solutions such as KCl and KNO_3 concentration in the range 1–7 mmol L^{-1}. The values in Figure 3(b) show that the presence of increased concentration of electrolyte can increase the micelle size and aggregation amount and a decrease in the equilibrium temperature is observed, but the critical micelle concentration (CMC) remains stable. Besides, inorganic salts enhance the hydrophobic interactions among surfactant aggregates and analytes. The obtained results indicate that both electrolyte solutions can affect the UA-CPE. However, the best analytical signal was provided at a KCl concentration of 5.0 mmol L^{-1} with a significant sensitivity difference. Therefore, 5.0 mmol L^{-1} KCl was chosen as optimal value.

3. 5. Effects of Equilibrium Temperature and Incubation Time

In this study, equilibrium temperature and incubation time were also optimized. In order to obtain the maximal preconcentration factor from sample volume of 15 mL, the UA-CPE should be performed at temperatures higher than the determined temperature for cloud-point. The effect of equilibrium temperature for Triton X-114 was studied in range of 30–60 °C under ultrasonic power (300 W, 40 kHz). The matrix became blurry when the solutions were placed in the ultrasonic bath with temperature equal to and higher than 30 °C due to its low cloud point temperature (23 °C), and the temperature had a notable effect on the extraction yield and the analytical signal was maximal in temperature range of 45–50 °C. Figure 4(a) shows that the absorbance of the analyte reaches maximum in 50 °C. The decrease in absorbance at temperature higher than 50 °C is likely due to the dissociation of the metal-chelate complex. Therefore, 50 °C was selected as the optimal temperature. The effect of incubation time on UA-CPE at 50 °C was studied within the range of 1–20 min in order to attain the equilibrium between two phases. From results in Figure 4(b), it is clear that an incubation time of 10 min is enough for quantitative extraction of analyte by UA-CPE.

The effect of centrifugation time at 4000 rpm was studied for time interval 5–20 min. It was found that a centrifugation time of 15 min was sufficient for efficient phase separation.

3. 6. Effect of Viscosity

Since the surfactant-rich phase provided by UA-CPE is quite viscous, in order to facilitate the detectability of samples by spectrophotometer, the viscosity must be reduced by addition of a diluent into the surfactant-rich phase. To establish the most suitable diluent, several organic solvents such as THF, acetone, acetonitrile, ethanol and methanol was investigated. From calibration curves constructed between absorbance and vanadium concentrations of 10, 20, and 40 µg L^{-1} with a wavelength difference ranging from 3 to 15 nm, ethanol gave the best analytical sensitivity (m/s, where m and s, respectively, are the slope of calibration curve and standard deviation of measurement) and was found to be suitable for dilution of surfactant-rich phase. Therefore, the surfactant-rich phase was diluted to 1.5 mL using ethanol. At these conditions, the analytical signals were maximal and reproducible.

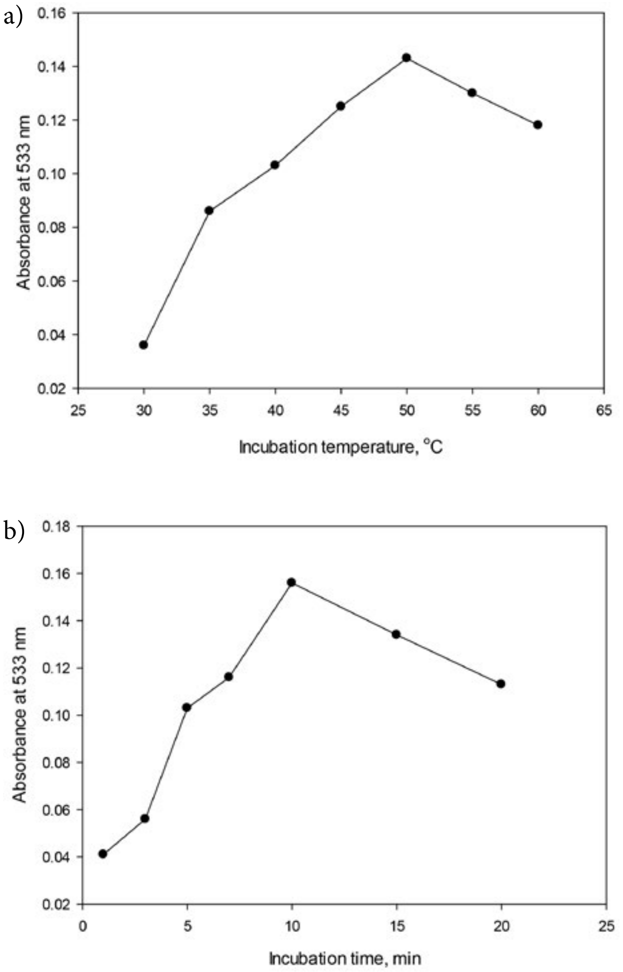

Figure 4. The influence of (a) incubation temperature and (b) incubation time at pH 6.0 on the analytical signal. Conditions: 50 µg L^{-1} V(V), 0.8 mmol L^{-1} B-R buffer at pH 6.0, 1.6 µmol L^{-1} pyrogallol, 2.0 µmol L^{-1} safranin T, 6.0 mmol L^{-1} KCl solution, and 0.05% (*w/v*) Triton X-114.

3. 7. Effect of Sample Volume

A significant amount of sample solution is necessary to provide the maximal enrichment factor in terms of a new method development. The compatibility with Beer's law was studied by monitoring the absorbance of serial solutions of V(V) in different concentrations. For this purpose, 3, 5, 10, 15, 20, 25, 30 and 35 mL of solutions containing 600 ng of V(V) were pretreated and extracted by UA-CPE under the optimal conditions. For this purpose, the sample volume was sequentially varied from 3 to 35 mL, the extraction was performed, the extract was diluted to 1.5 mL with ethanol, and the absorbance of each sample was measured against a sample blank. The results showed that by increasing the sample volume up to 15 mL, the extraction efficiency was gradually increased and became constant at higher volumes. Therefore, a sample volume of 15 mL was selected as optimal for maximal enrichment factor.

3. 8. Analytical Figures of Merit

Under the optimized conditions, as can be seen in Table 1, the limits of detection and quantification (LOD: $3s_{blank}/m$ and LOQ: $10\ s_{blank}/m$, in which the s_{blank} and m, respectively, are the standard deviation of ten replicate measurements of sample blank and slope of the calibration curve) of the method for V(V) were 0.58 and 1.93 µg L^{-1}, the recovery rates were in range of 93.8–103.2% (25 , 100 and 250 µg L^{-1}, n: 5), the precision (as RSD%) was in range of 2.6–4.1% (25, 100 and 250 µg L^{-1}, n: 5), the linear working range was 2–500 µg L^{-1}, and the sensitivity enhancement factor was 47.7 for enrichment or preconcentration of 15 mL sample by UA-CPE. The sensitivity enhancement factor was calculated from the slopes of the calibration curves established after and before preconcentration, in which the linear working range without preconcentration is 40–1200 µg L^{-1} with limits of detection and quantification of 9.1 and 30.3 µg L^{-1}. The corresponding linear regression equations after and before preconcentration are as follows:

$\text{Abs} = (2.29 \pm 0.20) \times 10^{-3}C[\text{V(V)}, \mu g\ L^{-1}] + (7.1 \pm 0.44) \times 10^{-3}$ with r^2: 0.9943 after preconcentration by UA-CPE,

Table 1. The analytical features of the proposed preconcentration method

Analytical parameters	**After preconcentration with UA-CPE**	**Before preconcentration with UA-CPE**
Linear working range, μg L^{-1}(n: 10)	2–500	40–1200
Intercept, b	$(7.1 \pm 0.44) \times 10^{-3}$	0.0135
Slope, m	$(2.29 \pm 0.20) \times 10^{-3}$	4.8×10^{-5}
Regression coefficient, r^2	0.9943	0.9965
Limit of detection, LOD μg L^{-1}	0.58	9.1
Limit of quantification, LOQ, μg L^{-1}	1.93	30.3
RSD % (25, 100 and 250 μg L^{-1}, n: 5)	2.6–4.1	2.35–3.80
Recovery % (25, 100 and 250 μg L^{-1}, n: 5)	93.8–103.2	96.5–101.5
Sample volume, mL	15	–
Consumptive index, mL	0.375	–
Enrichment or preconcentration factor*	40	–
Sensitivity enhancement factor**	47.7	–

*The factor, described as ratio of sample volume to consumptive index, in which the extraction and preconcentration of V(V) is quantitative for sample volume of 15 mL. **The ratio of slopes of the calibration curves with and without preconcentration with UA-CPE.

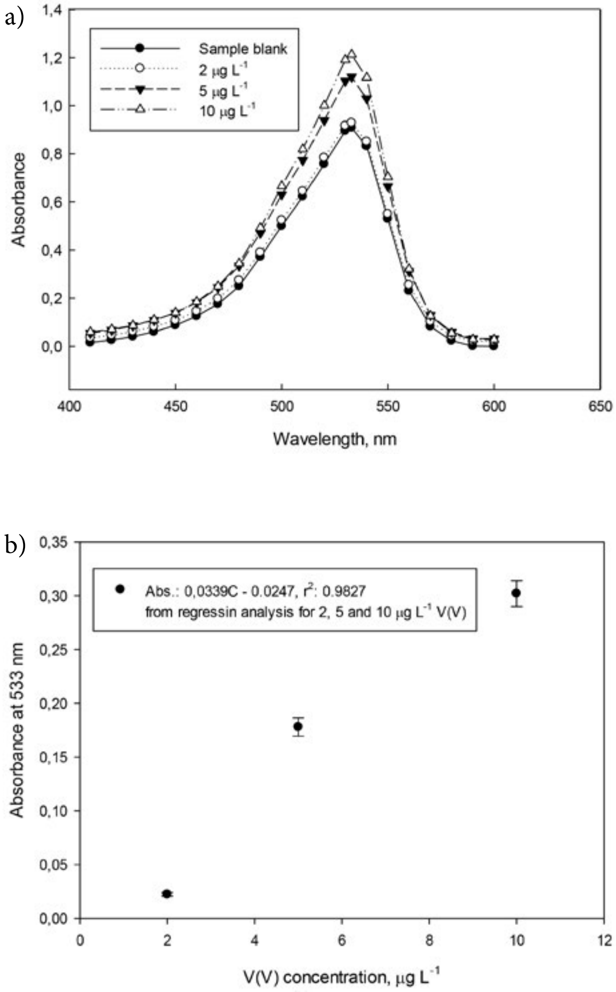

Figure 5. (a) The absorption spectra of the micellar system with increasing V(V) concentration at 2, 5 and 10 μg L^{-1} plus sample blank as a function of measurement wavelength (nm), λ_{max} (b) The linearity fit of the micellar system between V(V) concentration in range of 2–10 μg L^{-1} and absorbance corrected against sample blank at 533 nm.

Abs = 4.8×10^{-5} C [V(V), μg L^{-1}] + 0.0135 with r^2: 0.9965 before preconcentration.

Another variable that describes the preconcentration process, such as consumptive index (CI),[55] was determined. The consumptive index is described as the sample volume (mL), consumed to reach a unit of enrichment factor (EF): CI = V_{sample} (mL) / EF, where V_{sample} is the sample volume.

Under the optimal conditions, the absorption spectra of the micellar system, which has a maximum absorption at 533 nm, for three concentration levels of V(V) (2, 5 and 10 μg L^{-1}) including a sample blank is presented in Figure 5(a). Also, linearity fit with a sensitivity increase of 9-fold in slope of calibration for linear working range of 2–10 μg L^{-1} is given in Figure 5(b).

3. 9. The Matrix Effect

In this study, in order to show the selectivity of the method, the effect of possible interference of some metal ions on the quantitative analysis of V(V) (50 μg L^{-1}) was tested. The results obtained in this investigation are summarized in Table 2. A relative error of less than 5% was considered to be within the range of acceptable error. It is clear that interfering ions, which can potentially be found in environmental samples with tolerance ratio ranging from 25 to 1500, did not exhibit a matrix effect in determination of 50 μg L^{-1} of V(V) by this procedure. Therefore, it can be concluded that the developed method is fairly selective.

3. 10. The Analytical Applications of the Method

The analytical applicability of the developed UA-CPE method was checked by the quantitation of V(V) in

Table 2. The interfering effect of the possible matrix components on three replicate measurements of 50 μg L^{-1} of V(V) (n: 3)

Coexisting ions	**[Interferent] / [V^{5+}] ratio**	**Mean recovery ± *SD** * (%)**
Na$^+$, K$^+$, NH$_4^+$, Ca^{2+}, Mg^{2+}	1500:1	98.0 ± 2.5
Zn^{2+}	1250:1	101.0 ± 3.5
F$^-$, NO$_3^-$, Cl$^-$, Br$^-$, Mn^{2+}, Fe^{2+}	1000:1	97.2 ± 3.5
SO$_4^{2-}$, HPO$_4^{2-}$, HCO$_3^-$	750:1	98.0 ± 2.5
Cd^{2+}, Ag$^+$	600:1	97.5 ± 2.5
As^{3+}, Sb^{3+}, Mn^{2+}	500:1	96.0 ± 2.5
Ni^{2+}	500:1	101.5 ± 2.5
Pb^{2+}	400:1	97.5 ± 3.0
Formaldehyde, phenol	350:1	97.4 ± 2.0
Sn^{2+}, Al^{3+}	250:1	98.5 ± 2.5
Co^{2+}, Cr^{3+}	200:1	97.5 ± 2.5
NO$_2^-$, C$_2$O$_4^{2-}$	150:1	96.5 ± 3.0
HSO$_3^-$, Ascorbic acid	100:1	94.5 ± 2.5
V^{4+}, Sn^{4+}	75:1	101.0 ± 2.5
Fe^{3+}, Cu^{2+}	50:1	98.1 ± 3.0
Mo^{6+}	25:1	95.5 ± 2.5

* The percent recoveries plus standard deviations obtained from three replicate measurements of binary mixtures

Table 3. (a) The verification of the method accuracy by the replicate measurements of total V levels in the selected CRMs without and with spiking at levels of 5 and 15 μg L^{-1} after pretreatment and dilution (n: 5)

The CRMs	**Certified value, μg L^{-1} or μg kg^{-1}**	**After wet digestion with mixture of conc. HNO$_3$-H$_2$O$_2$ (3:2, v/v) at 130°C**				**After ultrasonic-assisted extraction with mixture of 4.0 mol L^{-1} HNO$_3$-4.0 mol L^{-1} HCl-0.5 mol L^{-1} H$_2$O$_2$ (1:1:1, v/v) at 60°C**				****The one-paired t-test**
		Added	***Found**	**RSD %**	**Recovery %**	**Added**	***Found**	**RSD %**	**Recovery %**	
SRM 1643e	37.86 ± 0.59 μg L^{-1}	–	38.5 ± 0.7	1.8	–	–	37.6 ± 0.6	1.6	–	2.04, 0.97
Trace elements		5	43.2 ± 0.8	1.9	94.0	5	42.3 ± 0.8	1.9	98.0	–
in water		15	53.1 ± 1.0	1.9	97.3	15	52.4 ± 1.0	1.9	99.3	
SRM 1515	***52 ± 3 μg kg^{-1}	–	50.8 ± 2.1	4.1	–	–	51.5 ± 2.0	3.9	–	1.28, 0.56
Apple leaves	after dilution at	5	55.4 ± 2.2	4.0	92.0	5	56.2 ± 2.1	3.7	94.0	–
	1:5 ratio	15	65.3 ± 2.3	3.5	97.0	15	66.2 ± 2.2	3.3	98.0	–

* The mean values plus their standard deviations of five replicate measurements ** The tabulated t-value is 2.78 for degree of freedom of 4 at 95% confidence interval for the statistical comparison of the mean values obtained by two analytical methods with certified value *** Where the certified value is 260 ± 30 μg kg^{-1} (k: 2.0 for 95% confidence interval)

Table 3. (b) The reproducibility and repeatability for the replicate measurements of total V in quality control samples spiked with 5, 10 and 15 μg L^{-1} (n: 5)

Samples	**Spiked concentration, μg L^{-1}**	**Intra-day precision**			**Inter-day precision**		
		***Found**	**Recovery%**	**RSD%**	***Found**	**Recovery%**	**RSD%**
Semi-skimmed	–	14.8 ± 0.5	–	3.4	14.5 ± 0.6	–	4.1
milk	5	19.5 ± 0.6	94.0	3.1	19.1 ± 0.6	92.0	3.1
	10	24.6 ± 0.7	98.0	2.8	24.0 ± 0.7	95.0	2.9
	15	29.6 ± 0.8	99.0	2.7	29.1 ± 0.8	97.0	2.7
Apple vinegar	–	55.8 ± 2.0	–	3.6	55.5 ± 2.2	–	4.0
	5	60.5 ± 2.1	94.0	3.5	60.0 ± 2.2	90.0	3.7
	10	65.4 ± 2.2	96.0	3.4	65.0 ± 2.3	95.0	3.5
	15	70.5 ± 2.3	98.0	3.3	70.1 ± 2.4	97.0	3.4

*The mean values plus their standard deviations of five replicate measurements beverages in contact with plastic products. The standard calibration curve was used in sample analysis. The accuracy and the validity of the extraction process was checked and verified by analysis of two standard reference materials, SRM 1515 Apple leaves and SRM 1643e Trace elements in water, representing the sample matrix. These data are summarized in Table 3(a). The obtained results were statistically in good agreement with the certified values with and without dilution. Also, the intra-day and inter-day precision studies for reliability of the results were conducted for the five replicate measurements of vanadium in quality control samples spiked with 5, 10 and 15 μg L^{-1}, shown in Table 3(b). The intra-day and inter-day precision (as RSD%) have been in range of 2.7–4.1% and 2.7–3.6% for the selected sample matrices, apple vinegar and semi-skimmed milk, respectively, while the recovery rates from spiked samples are in range of 94.0–99.0% and 92.0–97.0%.

Finally, the method after preconcentration with UA-CPE was applied to the determination of trace V(V) in some beverage samples after pretreatment with two different digestion procedures. The obtained results and the recoveries for the spiked samples are presented in Table 4. These results demonstrate that the recoveries for the spiked samples are in range of 95–98% with a lower RSD than 4.6%. When the mean values obtained by two analytical digestion approaches are compared, it can be seen that the experimental t-values (0.16–1.15) are statistically lower than the tabulated t-value of 2.31 for degree of freedom of 8 at 95% confidence interval, so as not to show a significant difference between the results. These results clearly indicate that the developed method can be reliably applied to the analysis of the selected beverage samples without any matrix effect.

3. 11. Comparison to Other Reported Preconcentration Methods

A comparison of the method performance with those of other preconcentration methods in literature for vanadium determination in beverage samples is given in Table 5. Apparently, the presented method has low LOD

Table 4. The results of total V analysis in beverages in contact with plastic products (n: 5)

Samples	After wet digestion with mixture of conc. HNO_3-H_2O_2 (3:2, v/v) at 130ºC				After ultrasonic-assisted extraction with mixture of 4.0 mol L^{-1} HNO_3-4.0 mol L^{-1} HCl-0.5 mol L^{-1} H_2O_2 at 60ºC				**The two-paired t-test
	Added, μg L^{-1}	*Found, μg L^{-1}	RSD%	Recovery%	Added, μg L^{-1}	*Found, μg L^{-1}	RSD%	Recovery%	
Semi-skimmed milk	–	15.1 ± 0.6	4.0	–	–	14.8 ± 0.5	3.4	–	0.23
	10	24.7 ± 0.8	3.2	96.0	10	24.5 ± 0.7	2.9	97.0	–
Buttermilk	–	14.3 ± 0.5	3.5	–	–	14.1 ± 0.5	3.5	–	0.22
	10	23.8 ± 0.8	3.4	95.0	10	23.8 ± 0.7	2.9	97.0	–
Grape vinegar1	–	56.4 ± 2.0	3.5	–	–	56.1 ± 2.0	3.6	–	0.16
	10	66.1 ± 2.2	3.3	97.0	10	65.8 ± 2.1	3.2	97.0	–
Apple vinegar1	–	75.5 ± 2.5	3.3	–	–	75.2 ± 2.4	3.2	–	0.20
	10	85.2 ± 2.6	3.1	97.0	10	84.8 ± 2.5	2.9	96.0	–
Grape vinegar2	–	36.7 ± 1.2	3.3	–	–	36.4 ± 1.2	3.3	–	0.40
	10	46.3 ± 1.4	3.0	96.0	10	46.1 ± 1.3	2.8	97.0	–
Apple vinegar2	–	42.3 ± 1.5	3.5	–	–	39.8 ± 1.4	3.5	–	0.48
	10	51.8 ± 1.6	3.1	95.0	10	49.5 ± 1.5	3.0	97.0	–
Pomegranate	–	13.8 ± 0.6	4.3	–	–	13.5 ± 0.5	3.7	–	0.36
	10	23.5 ± 0.8	3.4	97.0	10	23.1 ± 0.7	3.0	96.0	–
Orange juice	–	39.3 ± 1.3	3.3	–	–	38.8 ± 1.3	3.4	–	0.48
	10	48.8 ± 1.5	3.1	95.0	10	48.6 ± 1.5	3.1	98.0	–
Apricot juice	–	35.5 ± 1.2	3.4	–	–	35.2 ± 1.2	3.4	–	0.39
	10	45.2 ± 1.5	3.3	97.0	10	44.8 ± 1.4	3.1	96.0	–
Cherry juice	–	14.3 ± 0.5	3.5	–	–	14.0 ± 0.5	3.6	–	0.41
	10	24.0 ± 0.8	3.3	97.0	10	23.7 ± 0.8	3.4	97.0	–
Apple soda	–	15.7 ± 0.6	3.8	–	–	15.5 ± 0.6	3.9	–	0.79
	10	25.5 ± 0.8	3.1	98.0	10	25.2 ± 0.8	3.2	97.0	–
Lemonate soda	–	10.6 ± 0.4	3.8	–	–	10.3 ± 0.4	3.0	–	0.70
	10	20.2 ± 0.7	3.5	96.0	10	20.0 ± 0.6	3.0	97.0	–
Banana flavored milk	–	8.6 ± 0.4	4.6	–	–	8.3 ± 0.3	3.6	–	1.15
	10	18.3 ± 0.6	3.3	97.0	10	18.0 ± 0.5	2.8	97.0	–
Cherry flavored milk	–	9.5 ± 0.4	4.2	–	–	9.6 ± 0.4	4.2	–	0.71
	10	19.2 ± 0.7	3.6	97.0	10	19.3 ± 0.6	3.1	97.0	–

* The mean values plus their standard deviations of five replicate measurements ** Based on statistical comparison of the mean values obtained by two analytical digestion approaches, in which the tabulated t–value is 2.31 for degree of freedom of 8 at 95% confidence interval.

(0.58 μg L^{-1}), wide linear range (2–500 μg L^{-1}), minimal solvent consumption, quantitative recovery (93.8–103.2%), good accuracy (2.6–4.1%) and precision (2.4–4.1%), short analysis time (13 min), high sensitivity enhancement factor (47.7) and reasonable enrichment factor (40) from preconcentration of 15 mL of sample, and these analytical features are comparable or even better than those of most of the other preconcentration methods in Table 5. The combination of the UA-CPE with spectrophotometry as an alternative to the other previously reported detection techniques such as FAAS, ET-AAS, GF-AAS and ICP-OES offers several advantages including simplicity, easy to use, inexpensiveness, high recoveries, high preconcentration factor, and great extraction yield. The proposed method provides advantages such as wider linear working range, lower limit of determination, and precision with a reasonable sensitivity enhancement factor.

4. Conclusions

In this study, a new, accurate, precise, sensitive and selective UA-CPE procedure for extraction and preconcentration of trace vanadium present in the selected beverages using safranin T and pyrogallol at pH 6.0 has been reported before its determination by spectrophotometry at 533 nm. The UA-CPE procedure is simple, easy to use, safe, rapid, eco-friendly and inexpensive preconcentration tool. After separation and preconcentration of analyte from sample matrix, spectrophotometry at 533 nm as detection tool, which does not require expert user in his/her area and that can be readily accessible in almost every analytical research laboratory, was reliably used to monitor the vanadium levels in sample matrix. The method allows detection of vanadium at levels of 0.58 μg L^{-1} with sensitivity enhancement of 47.7, thus it can be used as an alternative to other analytical methods in the monitoring of free vanadium in the complex samples. The method was successfully applied to the extraction, preconcentration and determination of total V (as V(V) selected as analyte) in beverage samples after pretreatment with acid mixture, and satisfactory results were obtained.

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6. References

1. T. S. Anirudhan, P. G. Radhakrishnan, *Chem. Eng.* J **2010**, *165*, 142–150. **DOI:**10.1016/j.cej.2010.09.005

Table 5. The analytical performance data obtained by using UA-CPE coupled to spectrophotometry and other reported techniques in determination of vanadium in the selected beverage samples

Detection	**Preconcentration procedure**	**Linear working range, μg L^{-1}**	**LOD, μg L^{-1}**	**Preconcentration factor or enhancement factor**	**RSD %**	**Sample consumption, mL**	**Analysis time, min**	**References**
Spectrophotometry	SPE	110–3000	0.07	90	2.1	450	–	[22]
GF-AAS	CPE	2–50	0.05	100	5.8–7.5	50	75	[24]
Spectrophotometry	CPE	10–100 for V(IV), 1–70 for V(V)	0.12, 0.037	159, 99	0.67	10	55	[25]
Spectrophotometry	CPE	0.5–10 mg L^{-1}	0.113 mg L^{-1}	50	3.40	10	50	[26]
Spectrophotometry	CPE	0.05–0.6 mg L–1	5.51	20, 15	2.43	5	12	[27]
Spectrophotometry	CPE	up to 510	0.7	90	2.1	40	≥120	[28]
GF-AAS	CPE	1.0–60	0.05	20	3.9	10	10	[6]
FIA/Catalytic fluorimetry	CPE	0.02–10	0.007	50	1.8	10	25	[32]
ET-AAS	Ion-exchange	0–2	0.02	–	3.2	50	17	[20]
FAAS	UA-CPE	5–250	1.55	115	3.5	50	25	[34]
HR-CS-GFAAS	CPE	1–50	0.13	13.3	2.5	–	35	[29]
Spectrophotometry	SFDOME	3–100	0.94	38	3.90	50	20	[37]
Spectrophotometry	UA-CPE	2–500	0.58	47.7[a], 40[b]	2.6–4.1	15	13	The present method

Notes: (a) The sensitivity enhancement factor is the slope ratio of calibration curves after and before extraction; (b) ratio of the aqueous phase to final volume of eluent phase; FAAS: flame atomic absorption spectrometry; SPE: solid phase extraction; CPE: cloud point extraction,; GFAAS: graphite furnace atomic absorption spectrometry; ET-AAS: electrothermal atomic absorption spectrometry; UA-CPE: ultrasound assisted-cloud point extraction; ICP-OES: inductive coupled plasma optical emission spectrometry; FIA/Catalytic fluorimetry: flow injection analysis- catalytic fluorimetry; HR-CS-GFAAS: high resolution continuous source graphite furnace atomic absorption spectrometry; SFODME: solidified floating organic drop microextraction

2. A. Padilla-Rodríguez, J. A. Hernández-Viezcas, J. R. Peralta-Videa, J. L. Gardea-Torresdey, O. Perales-Pérez, F. R. Román-Velázquez, *Microchem. J.* **2015**, *118*, 1–11. **DOI:**10.1016/j.microc.2014.07.011
3. B. Patel, G. E. Henderson, S. J. Haswell, R. Grzeskowiak, *Analyst* **1990**, *115*, 1063–1066. **DOI:**10.1039/an9901501063
4. D. G. Barceloux, *J. Toxicol. Clin. Toxicol.* **1999**, *37*, 265–278. **DOI:**10.1081/CLT-100102425
5. ATSDR, Draft toxicological profile for vanadium, Atlanta, 2009, 378 http://www.atsdr.cdc.gov/toxprofiles/tp58.pdf.
6. H. Filik, D. Aksu, *Food Anal. Methods* **2012**, *5*, 359–365. **DOI:**10.1007/s12161-011-9254-9
7. M. S. Dundar, H.B. Saglam, *Trace Elem. Electroly.* **2004**, *21*, 60–63. **DOI:**10.5414/TEP21060
8. P. L. Teissedre, M. Krosniak, K. Portett, F. Gasct, A. L. Waterhouset, J. J. Serranot, J. C. Cabanist, G. Crosto, *Food Addit. Contam.* **1998**, *15*, 585–591. **DOI:**10.1080/02652039809374685
9. Naeemullah, T. G. Kazi, M. Tuzen, *Food Chem.* **2015**, *172*, 161–165. **DOI:**10.1016/j.foodchem.2014.09.053
10. M. J. C. Taylor, J. F. van Staden, Review. *Analyst* **1994**, *119*, 1263–1276. **DOI:**10.1039/an9941901263
11. A. Adachi, K. Ogawa, Y. Tsushi, N. Nagao, T. Kobayashi, *Water Res.* **1997**, *31*, 1247–1250. **DOI:**10.1016/S0043-1354(96)00379-X
12. A. Gaspar, J. Posta, Fresenius *J. Anal. Chem.* **1998**, *360*, 179–183. **DOI:**10.1007/s002160050671
13. K. Fujiwara, T. Morikawa, K. Fuwa, *Bunseki Kagaku* **1986**, *35*, 361–367. **DOI:**10.2116/bunsekikagaku.35.4_361
14. C. C. Chery, K. De Crèmer, R. Cornelis, F. Vanhaecke, L. Moens, *J. Anal. At. Spectrom.* **2003**, *18*, 1113–1118. **DOI:**10.1039/B301682J
15. H. Liu, S. J. Jiang, *J. Anal. At. Spectrom.* **2002**, *17*, 556–559. **DOI:**10.1039/b111577b
16. R. S. S. Murthy, D. E. Ryan, *Anal. Chem.* **1983**, *55*, 682–684. **DOI:**10.1021/ac00255a023
17. P. P. Coetzee, J. L. Fischer, M. Hu, *Water SA* **2002**, *28*, 37–44. **DOI:**10.4314/wsa.v28i1.4865
18. S. Kawakubo, K. Ogihara, M. Iwatsuki, *Analyst* **1995**, *120*, 2719–2723. **DOI:**10.1039/an9952002719
19. F. Garcia-Sanchez, A. Navas, M. Santiago, F. Grases, *Talanta* **1981**, *28*, 833–837. **DOI:**10.1016/0039-9140(81)80025-2
20. I. López-García, P. Vinas, R. Romero-Romero, M. Hernández-Córdoba, *Talanta* **2009**, *78*, 1458–1463. **DOI:**10.1016/j.talanta.2009.02.045
21. F. Z. Xie, X. C. Lin, X. P. Wu, Z. H. Xie, *Talanta* **2008**, *74*, 836–843. **DOI:**10.1016/j.talanta.2007.07.018
22. L. Rostampour, M. A. Taher, *Talanta* **2008**, *75*, 1279–1283. **DOI:**10.1016/j.talanta.2008.01.045
23. A. N. Anthemidis, K. I. G. Ioannou, *Talanta* **2009**, *79*, 86–91. **DOI:**10.1016/j.talanta.2009.03.005
24. S. Khan, T. G. Kazi, J. A. Baig, N. F. Kolachi, H. I. Afridi, S. Kumar, A. Q. Shah and G. A. Kandhro *J. Iran. Chem. Soc.* **2011**, 8(4), 897–907. **DOI:**10.1007/BF03246545
25. Z. A. A. Khammas, Z. T. Ibrahim, K. J. Al-adilee *Int. Res. J. Pure & Appl. Chem.* **2015**, 8(1), 33–48. **DOI:**10.9734/IRJPAC/2015/16431
26. Z. A-A. Khammas, R. A. Rashid *Sci. J. Anal. Chem.* **2015**; 3(5), 61–70. **DOI:**10.11648/j.sjac.20150305.14
27. E. Ghasemi, M. Kaykhah *Anal. Mets.* **2015**, 31, 407–411.
28. T. S. Stefanova, K. K. Simitchiev, K. B. Gavazov *Chem. Pap.* **2015**, 69(4), 495–503.
29. G. M. Wuilloud, J. C. A. de Wuilloud, R. G. Wuillou, M. F. Silva, R. A. Olsina, L. D. Martinez, *Talanta* **2002**, *58*, 619–627. **DOI:**10.1016/S0039-9140(02)00366-1
30. V. S. Souza, L. S. G. Teixeira, M. A. Bezerra, *Microchemical Journal* **2016**, *129*, 318–324. **DOI:**10.1016/j.microc.2016.06.029
31. C. B. Ojeda, F. S. Rojas, *Anal. Bioanal. Chem.* **2009**, *394*, 759–782. **DOI:**10.1007/s00216-009-2660-9
32. E. K. Paleologos, M. A. Koupparis, M. I. Karayannis, P. G. Veltsistas, *Anal. Chem.* **2001**, *73*, 4428–4433. **DOI:**10.1021/ac010395k
33. Y. Liu, J. Xu, Y. Xue, J. Wang, Y. Chang, C. Xue, *J. Environ. Anal. Chem.* **2015**, *95*, 258–270. **DOI:**10.1080/03067319.2014.1002494
34. R. Gürkan, S. Korkmaz, N. Altunay, *Talanta* **2016**, *155*, 38–46. **DOI:**10.1016/j.talanta.2016.04.012
35. X. Zhu, Z. Zhu, S. Wu, *Microchim. Acta* **2008**, *161*, 143–148. **DOI:**10.1007/s00604-007-0762-7
36. T. Madrakian, A. Afkhami, R. Siri, M. Mohammadnejad, *Food Chem.* **2011**, *127*, 769–773. **DOI:**10.1016/j.foodchem.2010.12.144
37. S. Dadfarnia, A. M. H. Shabani, A. Mirshamsi *Turk. J. Chem.* **2011**, 35, 625–636.
38. P. Berton, E. M. Martinis, R. G. Wuilloud, *J. Hazard. Mater.* **2010**, *176*, 721–728. **DOI:**10.1016/j.jhazmat.2009.11.094
39. M. F. Silva, E. S. Cerutti, L. D. Martinez, *Microchim Acta* **2006**, *155*, 349–364. **DOI:**10.1007/s00604-006-0511-3
40. K. Zih-Perenyi, A. Lasztity, Z. Horvath, A. Levai, *Talanta* **1998**, *47*, 673–679. **DOI:**10.1016/S0039-9140(98)00106-4
41. J. Krakowiak, D. Lundberg, I. Persson, *Inorg. Chem.* **2012**, *51*, 9598–9609. **DOI:**10.1021/ic300202f
42. M. K. Islam, C. Tsuboya, H. Kusaka, S. Aizawa, T. Ueki, H. Michibata, K. Kanamori, *Biochim. et Biophys. Acta* **2007**, *1770*, 1212–1218.
43. A. Nakajima, *Talanta* **2002**, *57*, 537–544. **DOI:**10.1016/S0039-9140(02)00068-1
44. K. A. Kuliyev, N. A. Verdizade, *American J. Chem.* **2015**, *5*, 10–18.
45. R. C. Skevington A study of the organic complexes of oxovanadium (IV). Bachelor of Science Thesis, Wollongong University College, The University of New South Wales, Australia, 1968.
46. Gao Zhu-Qing, Cai Xiao-Dong, Cheng Lei-Lei, Ling Kai-Cheng *Adv. Mat. Res.* 2011,396–398, 2225–2229. **DOI:**10.4028/www.scientific.net/AMR.396-398.2225
47. G. B. Gavazov, Zh. Simeonova, A. Alexandrov *Russian J. Inorg. Chem.* 2001, 46(3), 427–431.
48. K. B. Gavazov, T. S. Stefanova *Croat. Chem. Acta 2014,* 87(3), 233–240. **DOI:**10.5562/cca2436
49. A. K. Jana, S. Rajavenii *Spectrochim. Acta A* 60 (2004) 2093–2097. **DOI:**10.1016/j.saa.2003.10.041

50. A. Niazi, A. Yazdanipour, J. Ghasemi, M. Kubista, *Spectrochim. Acta A* **2006**, *65*, 73–78. **DOI:**10.1016/j.saa.2005.09.030
51. R. P. Frankewich, W. L. Hinze, *Anal. Chem.* **1994**, *66*, 944–954. **DOI:**10.1021/ac00079a005
52. M. E. F. Laespada, J. L. P. Pavón, B. M. Cardero, *Analyst* **1993**, *118*, 209–212. **DOI:**10.1039/AN9931800209
53. F. Shemirani, M. Baghdadi, M. Ramezani, *Talanta* **2005**, *65*, 882–887. **DOI:**10.1016/j.talanta.2004.08.009
54. N. Baghban, A. M. H. Shabani, S. Dadfarnia, A. A. Jafari, *Croat. Chem. Acta* **2012**, *85*, 85–90. **DOI:**10.5562/cca1803
55. Z. L. Fang, VCH, New York, **1993**, 85–128.

Povzetek

Razvili smo novo ekstrakcijsko metodo s surfaktantom in s pomočjo ultrazvoka za predkoncentracijo in določitev V(V) v vzorcih pijač. Po tvorbi kompleksa s pirogalolom v prisotnosti safranina T pri pH 6,0 smo V(V) ione ekstrahirali kot ternarni kompleks v micelarno fazo Tritona X-114. Kompleks smo spremljali pri 533 nm s spektrofotometrijo. Ocenili smo učinek matrice na izkoristek ekstrakcije V(V) iz obogatenih vzorcev (koncentracija 50 µg L^{-1}). Pri optimalnih pogojih je bila meja zaznave 0,58 µg L^{-1}, meja določitve 1,93 µg L^{-1} pri linearnem območju 2–500 µg L^{-1} in s povečanjem občutljivosti 47,7 ter s predkoncentracijskim faktorjem 40 za predkoncentracijo iz 15 mL raztopine vzorca. Izkoristki iz obogatenih vzorcev so bili v območju 93,8–103,2% z relativnim standardnim odklonom od 2,6% do 4,1% (25, 100 in 250 µg L^{-1}, n: 5). Točnost smo preverili z analizo dveh certificiranih vzorcev in rezultati so se dobro skladali s certificiranimi vrednostmi. Natančnost znotraj dneva in med dnevi smo preverili z določitvijo ponovljivosti (3,3–3,4%) in obnovljivosti (3,4–4,1%) na petih ponovitvah analize V(V) v vzorcih za kontrolo kvalitete z dodanimi 5, 10 in 15 µg L^{-1} vanadija. Z razvito metodo smo uspešno določili koncentracije V(V) v sledovih v izbranih vzorcih pijač.