Advances in Sample Preparation 1 (2021) 100005

Contents lists available at ScienceDirect

Advances in Sample Preparation

journal homepage: www.elsevier.com/locate/sampre

Vitamin E determination in edible oils by reversed-phase dispersive liquid-liquid microextraction and screen-printed carbon electrodes

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ARTICLE INFO

Keywords:
Vitamin E
Edible oils
Reversed-phase dispersive liquid-liquid microextraction
Screen-printed electrodes

ABSTRACT

A novel simple, environmentally friendly and portable method to determine vitamin E in edible oils based on reversed-phase dispersive liquid-liquid microextraction combined with electrochemical detection using screen-printed carbon electrodes (SPCEs) has been developed. Vitamin E was extracted from oil samples into a 4 M HCl aqueous solution and determined by differential pulse voltammetry using SPCEs. The extraction conditions optimized by experimental design (i.e., Plackett–Burman and central composite designs) were: aqueous 4 M HCl extractant volume, 43 μL; extraction time, 2 min; centrifugation time, 10 min; and centrifugation speed, 3000 rpm. The proposed method requires a standard addition calibration approach, and the working range showed good linearity from 0 to 20 mg L^{-1}, with a correlation coefficient ranging from 0.990 to 0.995 (N=5). The methodological limit of detection was between 1 and 3 mg L^{-1}. The repeatability of the proposed method was evaluated at 15 mg L^{-1}, and the relative standard deviation ranged between 10 and 15% (n=5). For the quantification of vitamin E in ten commercial samples of olive, sesame, soybean, sunflower and a mixture of sunflower and corn oils, the volume of the extractant phase (i.e., 4 M HCl aqueous solution) was increased up to 100 μL and satisfactory recoveries were obtained in the range of 85–115%, confirming the applicability of the method.

1. Introduction

Mediterranean diets, consisting of different kind of fruits, vegetables, grains and oils, are well known for their health benefits. Certain types of olive, sunflower, sesame and soybean oils are rich in lipid soluble antioxidants, such as vitamin E, which represent an essential component in human nutrition. There are eight isoforms of vitamin E, namely α-, β-, γ- and δ-tocopherol and α-, β-, γ- and δ-tocotrienol. The α-tocopherol form is the dominant isoform of vitamin E [1]. The necessity of using oils with a high content of vitamin E is associated with a decreased risk of developing and the prevention of Alzheimer's disease [2,3], amyotrophic lateral sclerosis [4] and chronic and acute diseases, such as cardiovascular, eye, bone, nephrological and neurological diseases, as well as osteoporosis and immune disorders [5].

Rapid and reliable analytical methods are required for the evaluation of the amount of vitamin E in vegetable oils, both for food quality control and in relation to studies on human health benefits. Most of the reported methods include chromatographic or electrophoretic techniques coupled to different detectors, such as electrochemical, ultraviolet-visible, fluorimetric or mass spectrometry [6–13]. However, these methods have major drawbacks; they are expensive and require bulky instrumentation and long analysis time. In this regard, electrochemical methods appear as an attractive alternative, since they can provide rapid and sensitive analysis using inexpensive and portable instrumentation. Vitamin E has been determined in edible oils by electroanalytical techniques, using electrodes mainly based on carbon materials (e.g., glassy carbon, carbon fibers) [14–18]. Additionally, screen-printed electrodes (SPEs) and ultramicroelectrodes based on platinum have been employed for this same purpose [19,20]. SPEs are designed to analyze low sample volumes, and include three electrodes (working, reference and counter electrode) in the same device. In addition, SPEs are mass-produced at low cost and are thus disposable. Considering such remarkable advantages, SPEs have received a widespread acceptance in major fields of analytical chemistry, including food analysis [21].

The complex matrix and particular properties of the different types of oils make sample treatment before instrumental analysis necessary. Solid-phase extraction [6,9,15], liquid-liquid extraction [8,12] and sample dilution with large amounts of organic solvents [7,11,13,15,17,19,22] have been the most commonly used procedures to prepare oil samples before chromatographic, electrophoretic or electrochemical analysis. However, these procedures have certain disadvantages, since they are highly time-consuming and involve the consumption of large amounts of toxic organic solvents. According to today's requirements, new analytical procedures should satisfy the principles

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https://doi.org/10.1016/j.sampre.2022.100005
Received 18 November 2021; Received in revised form 14 January 2022; Accepted 16 January 2022

of Green Analytical Chemistry [23]. Liquid-phase microextraction techniques fulfil some of these principles and have received great consideration among the scientific community [24]. In recent years, dispersive liquid-liquid microextraction (DLLME) has become one of the most widely employed analytical methods [25]. In conventional DLLME, analytes are extracted from an aqueous sample into an organic solvent. However, for the analysis of oily samples, so-called reversed-phase dispersive liquid-liquid microextraction (RP-DLLME) has been developed [26]. In this technique, a small volume of water (or aqueous solution with adjusted value of pH and ionic strength) replaces toxic solvents as the extractant phase. The aqueous extractant phase is dispersed into the organic sample using a moderately polar solvent as a dispersant [26], vortex agitation [27], or ultrasonic energy [10]. After centrifugation, the sedimented phase is an aqueous micro-drop that contains the target analytes and can be directly subjected to the detection step by analytical instrument. RP-DLLME offers several advantages, such as speed and ease of use, low cost, low sample volume, low solvent consumption, reduced generation of wastes, high enrichment factors and affordability.

RP-DLLME has been employed as a sample preparation technique prior to liquid chromatography-ultraviolet detection to determine vitamin E in edible oils [10]. However, to the best of our knowledge, the combination of RP-DLLME with SPEs for this aim has not been previously proposed. Therefore, in the present investigation we propose such a combination to develop an environmentally friendly procedure for rapid and sensitive determination of vitamin E in different edible oils (i.e., olive, sesame, soybean, sunflower and mixture of sunflower and corn oils). The method was optimized by experimental design, validated and applied to real samples. Finally, Eco-Scale metrics [28] were carried out in order to assess the greenness of the developed method.

2. Materials and methods

2.1. Reagents and oil samples

The α-tocopherol (Table S1) was obtained from Sigma-Aldrich (St. Louis, MO, USA). All reagents were of analytical reagent grade: n-hexane (97%) and methanol (99.9%) were also obtained from Sigma-Aldrich; sodium hydroxide (≥97%, pellets) was supplied by ACS Scharlau (Barcelona, Spain); acetone (99.5%) was purchased from Panreac Quimica SAU (Barcelona, Spain); hydrochloric acid (32%), dipotassium hydrogen phosphate (99.0%) and potassium dihydrogen phosphate (99.5%) were obtained from Merck (Madrid, Spain). The Milli-Q water (resistivity of 18.2 MΩ cm at 25 °C) used throughout the work was obtained using the Millipore Direct System Q5^{TM} purification system from Ibérica S.A. (Madrid, Spain).

A stock solution of 10 mg mL^{-1} of vitamin E was prepared by dissolving the appropriate amount of the reagent in acetone. The stock solution was prepared weekly due to the fast oxidation of the analyte. Working solutions were daily prepared by appropriate dilution of the stock solution in hexane. Oil samples (olive, sesame, soybean, sunflower and mixture of sunflower and corn oils) were purchased in a local supermarket (Alicante, Spain) and stored in a dark place at room temperature (21°C).

2.2. Apparatus and electrodes

Voltammetric measurements were performed using a Multi Autolab/M101 Potentiostat/Galvanostat from Metrohm Autolab B.V. (Utrecht, The Netherlands) controlled by Nova 1.10 software. The connector between the potentiostat and electrode (ref. DRP-DSC) was supplied by DropSens (Oviedo, Spain). Screen-printed carbon electrodes (SPCEs) (ref. DRP-110) with three-electrode configuration were obtained from DropSens. The electrodes consist of 4 mm diameter working and counter electrodes made of carbon. The reference electrode was made of silver.

A Vortex Reax Top shaker from Heidolph (Schwabach, Germany) and a Mixtasel-BL centrifuge from Selecta (Barcelona, Spain) were used to assist the extraction and phases separation, respectively.

2.3. RP-DLLME procedure

Fig. 1 shows the successive stages of the proposed RP-DLLME procedure for the extraction of vitamin E from oil matrix. 2 g oil sample was placed in a test tube and diluted with 3 mL of hexane. Next, 100 μL of aqueous 4 M HCl extractant phase was rapidly injected into the test tube. After vortex mixing for 2 min a cloudy solution was formed. The tube was then centrifuged at 3000 rpm for 10 min for complete phase separation. Finally, after removing the oily phase, the extractant phase (aqueous phase) was retrieved from the bottom of the test tube and deposited on the electrode surface for the voltammetric analysis.

2.4. Electrochemical analysis

Electrochemical study was undertaken using differential pulse voltammetry (DPV). A standard solution of 100 mg L^{-1} vitamin E in aqueous 1 M HCl was employed to optimize the DPV parameters, such as step potential, modulation time and interval time. In the potential range from 0 to +0.90 V and while maintaining modulation amplitude at 100 mV, the optimum values for step potential, modulation time and interval time were found to be 0.01 V, 0.05 s and 0.50 s, respectively. Under these conditions, an anodic peak corresponding to the oxidation of vitamin E appears at approximately +0.48 V (Fig. 1), and the height of this peak was employed for the quantification of the analyte. For each measurement, a new SPCE was used.

2.5. Data processing

A two-step multivariate optimization strategy, using Plackett–Burman and central composite designs, was carried out to determine the optimum conditions of the sample preparation procedure. NEMRODW® ("New Efficient Methodology for Research using Optimal Design") version 2007 software (Marseille, France) was employed to create the experimental design matrices and evaluate the results. The height of the anodic peak corresponding to vitamin E oxidation was employed as a response function during optimization experiments.

3. Results and discussion

3.1. Extractant phase optimization

The selection of the aqueous extractant phase plays an important role in the proposed procedure, since it affects both the extraction and the detection. The influence of the extractant phase composition and the pH on the electrochemical response of vitamin E was evaluated through direct analysis with SPCEs of 100 mg L^{-1} standard solutions in the following media: aqueous 1 M HCl (pH 0); mixture of methanol and water, acidified with acetic buffer solution to pH 4.5 in the ratio 80:20 (pH 4.5); phosphate buffer solution (dihydrogen phosphate/hydrogen phosphate) (pH 7.5); and 1 M NaOH (pH 14). As it can be observed in Fig. 2, the voltammetric signal was only achieved in aqueous 1 M HCl (Fig. 2a) and, therefore, HCl medium was selected for further studies. The obtained results were in agreement with a recent publication in which the highest peak current response of oxidation of vitamin E was obtained for measurements performed in the solutions of mineral acids at low pH in comparison with other electrolytes, such as buffers or alkaline solutions [18].

Afterwards, in order to evaluate the influence of the HCl concentration on the overall procedure, RP-DLLME was carried out from 5 mL hexane standards at 2 mg L^{-1} of vitamin E, varying the HCl concentration of the extractant phase from 1 to 5 M. The final acidic aqueous extracts were electrochemically analyzed with the SPCEs. At 5 M HCl,

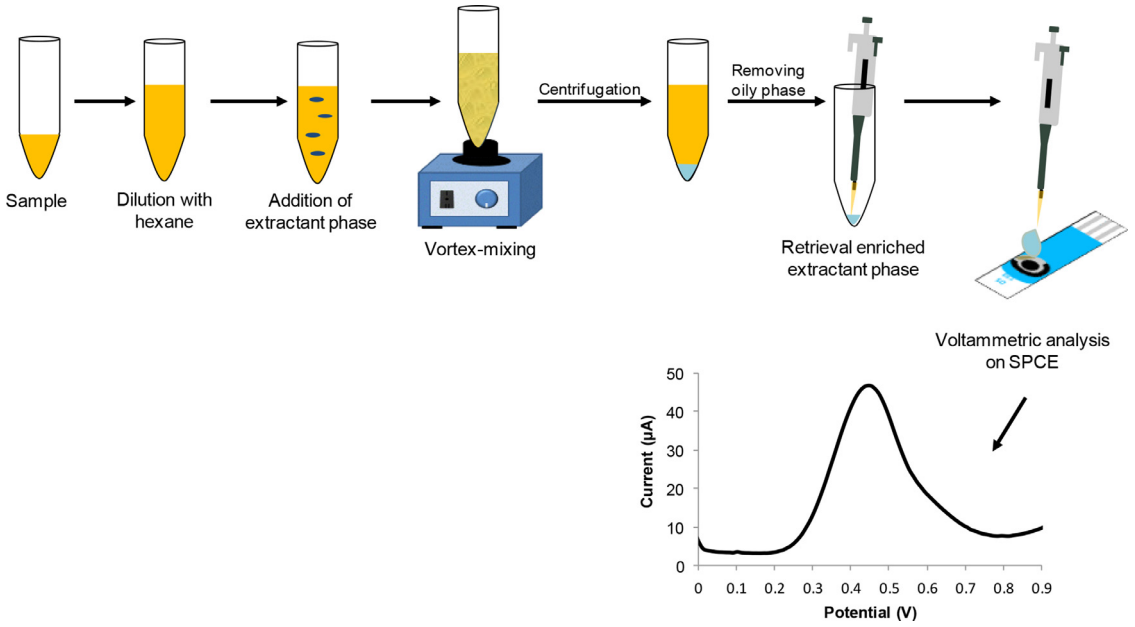

Fig. 1. The RP-DLLME procedure coupled with SPCE detection.

the drop of the extractant phase spread out of the electrode surface, and thus the electrochemical signal was not achieved at this concentration. On the other hand, the analytical signal demonstrated the highest value at 4 M HCl, with a relative standard deviation (RSD) of 14% (Fig. 3). The highest signal at 4 M HCl concentration could be attributed to an increase of hydrogen-bonding interactions and thus higher extraction performance. Therefore, 4 M HCl was finally selected as the optimum extractant phase for the proposed procedure.

3.2. Optimization of other parameters effecting the extraction

3.2.1. Screening step

When a large number of experimental factors might affect the results, it is necessary to appropriately optimize these factors and obtain measurements under the best possible conditions. Plackett–Burman is a two-level fractional factorial design which gives the possibility of identifying the main factors and evaluating their significance in a few experiments, which is time saving compared to one-at-a-time optimization [29]. Four experimental factors were studied with Plackett–Burman design, namely: aqueous 4 M HCl extractant volume, extraction time, centrifugation time and centrifugation speed. The effects of the four selected factors were investigated in eight experiments, which were randomly performed using 5 mL hexane standard solutions at 2 mg L^{-1} of vitamin E. The levels of the experimental factors considered in the Plackett–Burman design are shown in Table S2.

The data obtained were evaluated by analysis of variance (ANOVA) at a 95% confidence level, and *p*-test values ($p < 0.05$) showed the significance of the experiment. The correlation coefficient of the linear model was 0.995. According to the results obtained from the Plackett–Burman design, all studied factors were significant and a Pareto chart (Fig. 4) illustrates this, with effects exceeding the vertical reference lines. Aqueous 4 M HCl extractant volume and extraction time were significant factors with negative and positive effect, respectively; therefore, these factors were studied in the next optimization step in order to set up the optimum conditions. Regarding centrifugation conditions, centrifugation time was fixed at the upper level, since it was long enough for phase separation and there was no reason to extend the procedure more than 10 min. Finally, centrifugation speed at the highest values promoted better phase separation, so in subsequent experiments it was also fixed at the upper level, with the conforming value 3000 rpm.

3.2.2. Central composite design

A two-factor central composite design [29] was used to evaluate and optimize the aqueous extractant volume and extraction time. Thirteen experiments, including five replicates at the central point, were randomly performed using 5 mL hexane standard solutions with 2 mg L^{-1} of vitamin E. Table S3 shows the low and high levels, the central and star points of the considered factors in the optimization step.

According to the response surface (Fig. 5a), fitting the second-grade polynomial model, and the contour plot (Fig. 5b), the highest signals were obtained for low extractant volume and low extraction time, and for high extractant volume and high extraction time. The former case could be explained considering that a minimal volume of aqueous extractant phase led to a higher concentration of the target analyte, whereas a lower extraction time revealed that equilibrium was reached in a few minutes. In addition, it should be noticed that for 43 µL of extractant phase, the system response obtained at different times (i.e., 2–8 min) could not be considered significantly different (Fig. 5b). On the other hand, for higher extractant volume, the time needed to reach the equilibrium is higher and, therefore, analyte signal increased with time in this case. Finally, 43 µL of extractant phase and 2 min of extraction were selected as optimum values in order to reduce the time of the extraction procedure.

In summary, the results obtained after optimization gave the possibility of establishing the following optimum conditions: aqueous 4 M HCl extractant volume, 43 µL; extraction time, 2 min; centrifugation speed, 3000 rpm; and centrifugation time, 10 min.

3.3. Analytical figures of merit

Under the optimized experimental conditions, a calibration curve was constructed using 5 mL hexane standards over a range of concentrations from 1.0 to 100 mg L^{-1} of vitamin E (N=6). However, in the recovery study, diluted oil samples and diluted oil samples spiked at 20 mg L^{-1} with vitamin E were analyzed and recoveries, calculated as $(C_{spiked\ sample}\text{-}C_{unspiked\ sample})/C_{added}$ x 100, provided values of 190% for the mixture of sunflower and corn oils; 136 and 111% for two sunflower oils (S1 and S2, respectively); 28 and 183% for two virgin olive oils (S1 and S2, respectively); 245 and 179% for two olive oils (S1 and S2, respectively); 84% for extra virgin olive oil; 237% for soybean oil; and 120% for sesame oil. Therefore, the results obtained revealed that the

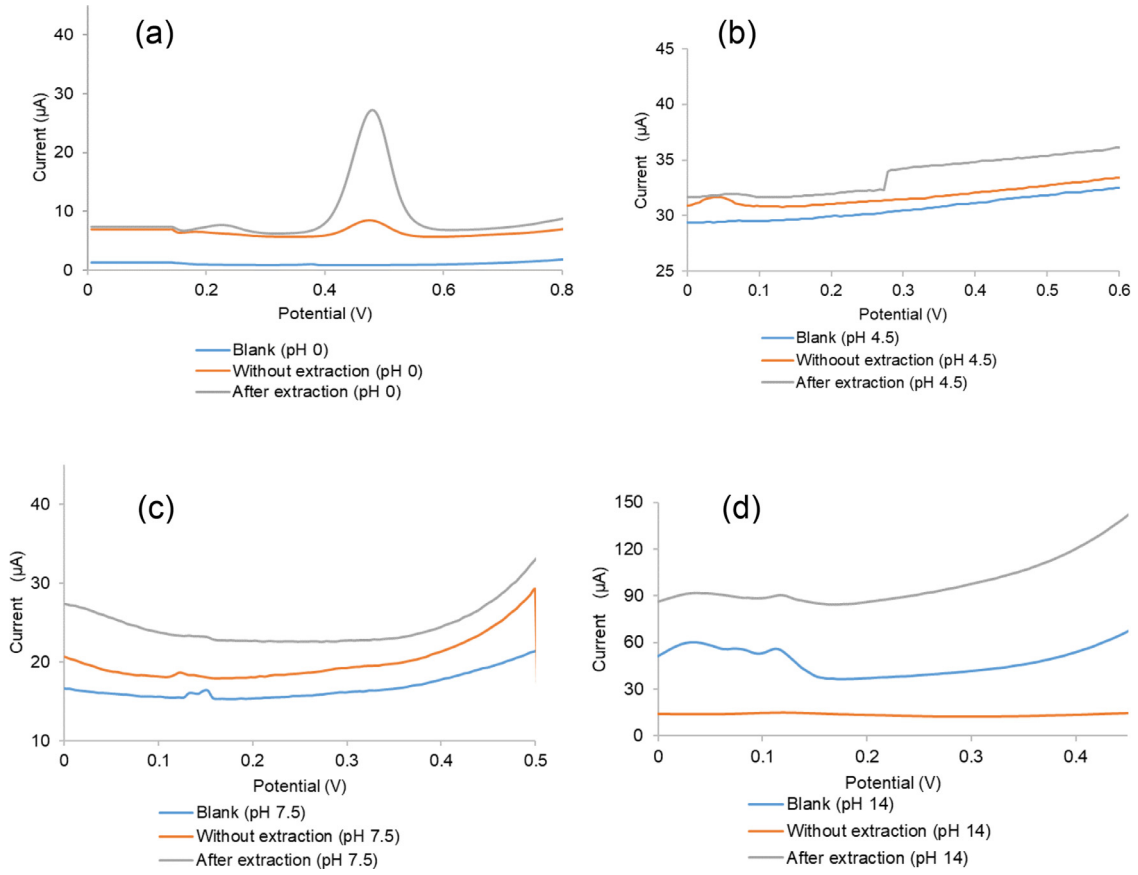

Fig. 2. Selection of the extractant phase. (a) HCl (pH=0); (b) MeOH:H_2O (80:20, pH=4.5); (c) Phosphate buffer (pH=7.5); and (d) NaOH (pH=14). (Conditions without extraction: 100 mg L^{-1} of vitamin E in the indicated mediums. Extraction conditions: extraction from 5 mL hexane standards at 2 mg L^{-1} spiking level of vitamin E, 100 μL of extractant phase, 1 min of extraction time and 5 min of centrifugation at 3000 rpm).

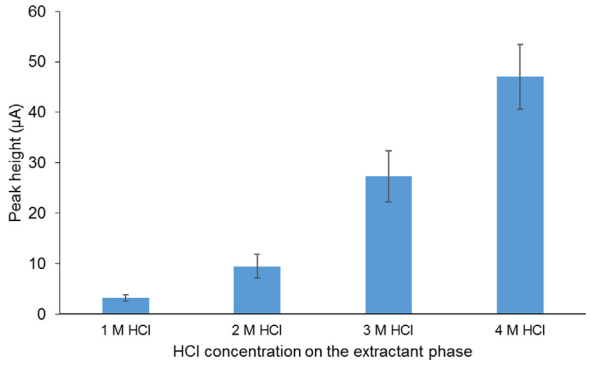

Fig. 3. Effect of the HCl concentration on the extractant phase. (Conditions: extraction from 5 mL hexane standards at 2 mg L^{-1} spiking level of vitamin E, 100 μL of extractant phase, 3 min of extraction time and 10 min of centrifugation at 3000 rpm). Error bars represent the standard deviation of three replicated analysis.

different oil matrices had a significant effect (positive or negative) on the analysis. Thus, considering the strong matrix effects, a standard addition calibration strategy was applied to all oil samples. To this end, ten edible oil samples were investigated and calibration curves were constructed using standards of five concentration levels from 0 to 20 mg L^{-1}. The resulting standard addition calibration curves gave a high level of linearity with correlation coefficient (r) values ranging from 0.990 to 0.995. The sensitivity of the method estimated by the slope of the calibration curve ranged from 0.52±0.07 to 1.00±0.09 μA mg^{-1} L. RSD was studied by five consecutive extractions of each edible oil spiked at 15 mg L^{-1} and ranged between 10 and 15%, which shows good precision of the method. The methodological limit of detection (mLOD) [30] was statistically evaluated using three times the standard deviation of the peak heigh for each edible oil. Obtained in this way, mLOD values were between 1 and 3 mg L^{-1}. The methodological limit of quantification, defined as 3.3 times the mLOD [31], was from 3.3 to 10 mg L^{-1}. It should be noted that both mLOD and mLOQ were lower than the average content of vitamin E found in edible oil samples (Table 1).

The enrichment factor (EF) was found by the following strategy. First, a hexane standard containing 100 mg L^{-1} of vitamin E was subjected to the proposed method. Then, vitamin E was dissolved in aqueous 4 M HCl at the same concentration level (i.e., 100 mg L^{-1}), and this aqueous solution was directly analyzed by DPV with SPCEs. The EF was calculated as the signal ratio of the above-mentioned experiments and resulted in 6.

3.4. Analysis of edible oil samples

To demonstrate the applicability and reliability of the proposed method, it was applied to the determination of vitamin E in edible oil samples, namely: olive, sesame, soybean, sunflower and a mixture of sunflower and corn oils. Analyses were carried out on oil samples of 2 g diluted with 3 mL of hexane, unless otherwise stated in the text.

When RP-DLLME was performed on virgin olive oil samples, a thin solid layer was formed between the extractant phase and sample solution after centrifugation, which hindered the retrieval of the aqueous acceptor solution. We therefore decided to increase the volume of extractant phase from 43 μL to 100 μL for all oil samples in order to ensure

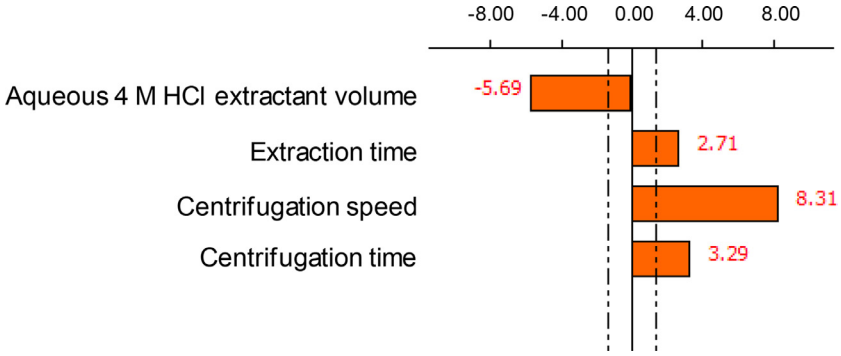

Fig. 4. Pareto chart of the Plackett–Burman design.

an easy to handle volume with real samples. On the other hand, virgin and extra virgin olive oil samples are rich in polyphenols that could potentially be extracted and interfere in vitamin E determination [32]. However, it was checked that, under the proposed extraction and detection conditions, polyphenols signal (i.e., ortho-phenols and tyrosol) did not interfere with the signal of vitamin E at +0.48 V.

Throughout the analysis of sesame oil, a precipitate sedimented in the bottom of the test tube and mixed with the aqueous extractant phase, hindering its retrieval even when using 100 µL. To overcome this problem, the sesame oil sample was reduced to 1 g and dissolved with 4 mL of hexane, further RP-DLLME was applied. After phase separation, the hexane-oil phase was carefully removed from the test tube and another 50 µL of aqueous 4 M HCl extractant phase was added to the residue. Then, it was centrifuged again at 3000 rpm for 10 min. After those steps, three phases (aqueous extractant, precipitate and the remains of oily phase) were completely separated in the bottom of test tube and, thus, the aqueous phase was easily withdrawn for electrochemical analysis [33].

In the recovery studies, diluted oil samples and diluted oil samples spiked at 20 mg L^{-1} with vitamin E were analyzed by the standard addition calibration strategy with calibration curves using standards containing 0, 5, 10, 15 and 20 mg L^{-1} of vitamin E. Table 1 summarizes the results obtained. As can be seen, recovery values ranged between 85 and 115%. Therefore, we can conclude that matrix effects were corrected for

Table 1
Added and found concentrations and recoveries obtained in edible oil samples.

Sample[a]	Concentration (mg L^{-1})		Recovery[c] (%)
	Added	Found±SD[b]	
Refined mixture of sunflower and corn oils	0	33±4	95
	20	52±9	
S1 - Refined sunflower oil	0	14±2	95
	20	33±5	
S2 - Refined sunflower oil	0	29±4	95
	20	48±7	
S1 - Virgin olive oil	0	14±4	85
	20	31±6	
S2 - Virgin olive oil	0	25±7	90
	20	43±7	
S1 - Olive oil	0	34±4	105
	20	55±11	
S2 - Olive oil	0	18±4	110
	20	40±7	
Extra virgin olive oil	0	10±2	100
	20	30±4	
Soybean oil	0	22±2	105
	20	43±6	
Sesame oil	0	27±7	115
	20	50±8	

[a] S1, S2 mean different commercial brands of the same kind of oil sample.
[b] SD: standard deviation of x-value estimated using regression line [31].
[c] Recovery calculated as: $(C_{spiked\ sample}-C_{unspiked\ sample})/C_{added}$ x 100.

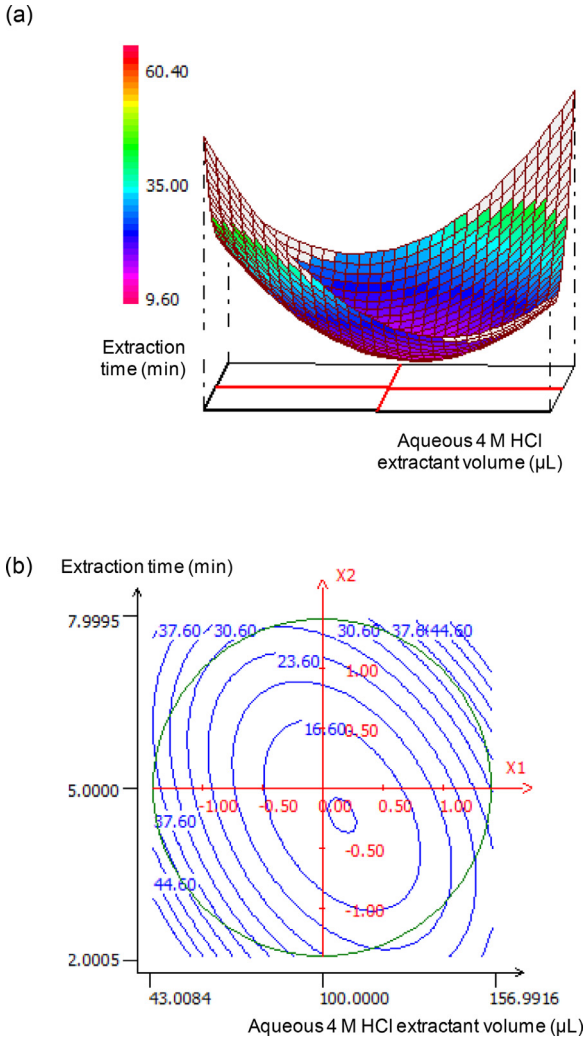

Fig. 5. (a) Response surface; and (b) contour plot of central composite design.

the selected oil samples using the standard addition calibration strategy, and the applicability of the proposed method is demonstrated. The concentration of vitamin E was 83±10 mg Kg^{-1}, 36±4 mg Kg^{-1} and 73±9 mg Kg^{-1} in the refined mixture of sunflower and corn oils and refined sunflower oil (S1 and S2, respectively), respectively. Concentrations of 35±11 mg Kg^{-1}, 63±17 mg Kg^{-1}, 84±10 mg Kg^{-1}, 45±9 mg Kg^{-1} and 25±6 mg Kg^{-1} of vitamin E were found in virgin olive oil (S1 and S2, respectively), olive oil (S1 and S2, respectively), and extra virgin olive oil, respectively. Soybean and sesame oil contained 55±5 mg Kg^{-1} and 140±30 mg Kg^{-1} of vitamin E, respectively.

Table 2
Comparison of the proposed method with other electrochemical methods for vitamin E determination in oil samples.

Sample preparation	Electrode	Electrochemical techique	LOD(mg L^{-1})	Ref.
Direct oil addition into the electrolyte	DNA-immobilized carbon nanotube electrode	SWASV (in phosphate buffer solution at pH=3.51)	0.00005	[14]
SPE (silica cartridge) of 0.6 g of oil. Elution with 10 mL of hexane. The eluate was mixtured with 0.5 mL of 0.1 M H_2SO_4 in ethanol, 3 mL of 0.5 M TMA in ethanol, 11.5 mL of ethanol, and hexane up to 25 mL	GCE	DPV	0.8	[15]
1.5 mL of oil dissolved in benzene:ethanol (1:2) with 0.1 mol L^{-1} H_2SO_4	Carbon fiber disk UME	SWV	5.0	[16]
0.3 g of oil sample dissolved in 5 mL of acetone, addition of 1.0 mL of 1.0 M [EMIM][NTf_2] in acetone	Nafion and electrochemically reduced graphene oxide-modified GCE	SWV	0.025	[17]
0.8 g of oil dissolved in 50 mL of 50% aqueous-acetonitrile mixture, extraction into silicone oil (acting as lipophilic binder of the electrode)	GCPE	SWASV (in 0.1 M HNO_3)	0.001	[18]
Dilution of olive oil sample with 2-propanol (1:10, v:v)	Pt-SPE	DPV	0.157	[19]
3 mL of oil dissolved in 1 mL of NMP and mixtured with 1 mL 0.04 M NBu_4PF_6 at 60°C	Pt disk UME	DPV	12.9	[20]
2 g of oil dissolved up to 5 mL with hexane and RP-DLLME into aqueous 4 M HCl	SPCE	DPV	1-3	This work

SWASV, square-wave anodic stripping voltammetry; SPE, solid-phase extraction; TMA, tetramethylammonium chloride; GCE, glassy carbon electrode; DPV, differential pulse voltammetry; UME, ultramicroelectrode; SWV, square-wave voltammetry; [EMIM][NTf_2], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; GCPE, glassy carbon paste electrode; Pt-SPE, screen-printed platinum electrode; NMP, *N*-methyl-pyrrolidone; NBu_4PF_6, tetrabutylammonium hexafluorophosphate; RP-DLLME, reversed-phase dispersive liquid-liquid microextraction; SPCE, screen-printed carbon electrode.

3.5. Comparison with other electrochemical methods

Previously reported electrochemical methods for determination of vitamin E in oil samples are presented in Table 2. The obtained mLOD using RP-DLLME-SPCE is of the same order than those obtained with other electrodes [15,16,20]. On the other hand, the works presenting higher sensitivity [14,17–19] needed an electrode preconditioning procedures before each measurement or use a more complex electrodic system compared with this methodology, in which there is no need to prepare or modify the electrode for each measurement due to they are low cost and disposable. Furthermore, the other methodologies employed a more complex sample prep procedure [15,18] or higher number of reagents or solvents, some of them toxics (i.e., benzene [16] or NBu_4PF_6 [20]), or tedious preparation electrode procedures (i.e., [14,17,18]) involving longer times [14].

Therefore, the RP-DLLME-SPCE procedure could be considered easier handling, simpler and environmentally friendly compared to the other previous methodologies (Table 2).

3.6. Analytical Eco-Scale

The analytical Eco-Scale is a comprehensive approach to evaluate the greenness of an analytical method [28]. The Eco-Scale is based on a scoring system which gives the maximum value (i.e., 100 points) to the ideal green analytical method. The reagents (amount and hazard), energy and wastes involved in an analytical method give penalty points, which are deducted from the maximum score, leaving a final score which reveals the grade of greenness of the developed method [28]. Table 3 shows the analytical Eco-Scale calculation of the proposed method for the analysis of an edible oil sample considering the standard addition calibration. According to the results, the combination of RP-DLLME with electrochemical analysis by SPCEs represents an acceptable green analytical method since the resulting score was between 50 and 75 points [28].

Table 3
Penalty points and analytical Eco-Scale total score for the proposed method (RP-DLLME-SPCE).

Reagents	Penalty points
Hexane (10-100 mL)	16
HCl 4 M (< 10 mL)	4
Vitamin E standard (< 10 mL)	4
Instruments	
Vortex (≤ 0.1 kWh)	0
Centrifuge (≤ 1.5 kWh)	1
Potentiostat (≤ 0.1 kWh)	0
Waste	5
Total penalty points	**30**
Analytical Eco-Scale total score	**70**

4. Conclusions

In this work a novel, rapid, economical and simple method for determining vitamin E in edible oils has been presented. The greenness of the combination of vortex-assisted RP-DLLME with electrochemical detection by SPCEs has been semi-quantitatively evaluated, revealing that the proposed method complies with the requirements of Green Analytical Chemistry. Multivariate optimization has been carried out to find out the best extraction conditions, reducing time, efforts, sample and reagents. Finally, the applicability of the method has been successfully proved with the analysis of different edible oils giving good recoveries. However, the developed methodology could present some limitations regarding the automatization due to some steps of the procedure. Therefore, further actions should be addressed to study its feasibility in order to implement the methodology as a quality control procedure of edible oils.

Acknowledgments

The authors would like to thank the Ministry of Science and Innovation of Spain (project no. CTQ2016-79991-R) and Generalitat Valenciana (Spain) (project nos. GVA/2014/096 and PROMETEO/2018/087) for the financial support. A.D. gratefully acknowledges the University of Alicante and the research group “Atomic-mass spectroscopy and analytical chemistry under extreme conditions” for giving the opportunity for implementation of the research project and the Scientific Grant Agency of the Ministry of Education of the Slovak Republic (VEGA 1/0220/21)

for financial support. E.F. also wishes to thank the Spanish Ministry of Education for her FPU grant (FPU13/03125). The authors extend their appreciation to Ministry of Science, Innovation and Universities for granting the Spanish Network of Excellence in Sample Preparation (RED2018-102522-T). This article is based upon work from the Sample Preparation Study Group and Network, supported by the Division of Analytical Chemistry of the European Chemical Society.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.sampre.2022.100005.

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