Air-Assisted Alkanol-Based Nanostructured Supramolecular Liquid–Liquid Microextraction for Extraction and Spectrophotometric Determination of Morin in Fruit and Beverage Samples

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Abstract

A new air-assisted liquid–liquid microextraction method based on alkanol nanostructured supramolecular solvents coupled to spectrometric analysis was developed for extraction, preconcentration, and spectrophotometric determination of morin. Al(III)-morin complex was performed at pH 4.5. Four different alkanol-based SUPRAS (supramolecular solvents) were prepared for the separation and preconcentration of Al-morin complex from aqueous solution by using vortex and centrifugation. Effect of analytical variables and tolerance limit of matrix ions were investigated. Under the optimum conditions, detection limit, quantification limit, relative standard deviation, preconcentration factor, and enhancement factor were found as 3.5 µg L^{-1}, 10 µg L^{-1}, 3.1%, 120, and 95, respectively. The accuracy of the method was performed with standard addition. The obtained results demonstrated the applicability of the method for the separation, preconcentration, and determination of morin in fruit and beverage samples. The method also complies with green chemistry principles as it uses green solvents, reduces reagent volumes, and produces low amounts of waste.

Introduction

Flavonoids are polyphenolic compounds that have important health effects such as antioxidant, antiviral, antiallergic, and anti-inflammatory (Hadjmohammadi et al. 2013; Pietta 2000; Cao et al. 1997; Arancibia et al. 2017). Some plants, vegetables, fruits, beverages, and food samples are rich with respect to flavonoids (Kokulnathan et al. 2018; Jiang et al. 2008). Flavonoids are beneficial for some diseases such as cancer, cardiovascular, diabetes, Alzheimer's, and rheumatoid arthritis (Sani et al. 2020; Chen and Chen 2013; Scalbert et al. 2005). There are many pharmaceutical samples containing flavonoids in the markets. Recent studies have reported that flavonoids have an important role in inhibiting key proteins involved in the coronavirus infection cycle (Russo et al. 2020). It is recommended that flavonoid intake decreases the risk of coronary heart disease and cardiovascular disease (Kim and Je 2017). Estimated daily intake of flavonoids has been reported as 165.6 mg day^{-1} for Chinese adults (Li et al. 2013) and 379.1 mg day^{-1} for US Adults (Huang et al. 2020). Morin (2-(2,4-dihydroxyphenyl)-3,5,7-trihydroxychromen-4-one) is an important flavonoid and it can interact with nucleic acids, proteins, enzymes, free radicals (Altunay et al. 2019). Morin is widely distributed in vegetables, fruits, and several Chinese herbs. The contents of morin in foodstuffs have been reported in range of 2–250 mg kg^{-1} in fruits, 3–13 mg L^{-1}

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in fruit juices, 0–100 mg kg⁻¹ in vegetables, 4–16 mg L⁻¹ in red wine, 10–25 mg L⁻¹ in tea, and 200–600 mg kg⁻¹ in onions, respectively (Hertog et al. 1992, 1993). Considering these properties, it is of great importance to develop a fast and reliable technique for the analysis of this compound in various samples such as biological, food, fruit, and vegetable.

Flavonoids including morin have been determined in different matrix by using analytical techniques such as spectrophotometer (Mayahi and Rajabi 2017), high-performance liquid chromatography (Hadjmohammadi et al. 2013), gas chromatography mass spectrometry (Fiamegos et al. 2004), capillary electrophoresis (Memon et al. 2018), electrooxidation (Ziyatdinova et al. 2014), and diffuse reflectance spectroscopy (Dmitrienko et al. 2012). The spectrophotometer includes some advantages such as efficiency, simplicity, ease of use, and cheapness. Moreover, it is readily available at routine laboratories. Direct determination of morin in fruit and beverage samples by using spectrophotometer is difficult due to the low detection limit of the instrument and the matrix effect. Various separation and preconcentration methods such as hollow fiber liquid-phase microextraction (Hadjmohammadi et al. 2013), ultrasound extraction (Qiao et al. 2011), solid-phase microextraction (Majidi and Hadjmohammadi 2019), ionic liquid dispersive microextraction (Altunay et al. 2019), deep eutectic solvent extraction (Nia and Hadjmohammadi 2019), dispersive magnetic solid-phase extraction (Sani et al. 2020), and air-assisted liquid–liquid microextraction (AA-LLME) (Farajzadeh and Mogaddam 2012) have been reported in the literature for increase the sensitivity of the instrument and decrease the matrix effects.

The AA-LLME technique was first applied in 2012 for the extraction and determination of phthalate esters in aqueous samples (Farajzadeh and Mogaddam 2012). Although this method is basically similar to dispersive liquid–liquid microextraction, no organic solvent is required to disperse an extractant into the sample solution. In this procedure, μL volumes of extraction solvent were dispensed into the sample solution by performing several suction/distribution cycles with the aid of a syringe equipped with a needle. With this procedure, the contact area of the extraction solvent with the sample solution increased significantly even though no dispersing solvent was used (Farajzadeh et al. 2020).

Supramolecular solvents (SUPRAS) are green and cheap for liquid–liquid microextraction (LLME) (Zohrabi et al. 2016). SUPRAS are water-immiscible nanostructured liquids and it provide different interactions such as ionic and hydrogen bonding with organic and inorganic analytes and hydrophobic increase to extraction efficiency (Yilmaz and Soylak 2014; Yang et al. 2017). Alkanol-based supramolecular solvents air-assisted liquid–liquid microextraction (SUPRAS-AA-LLME) method has some

advantages such as high efficiency, short extraction time, cost effective, and easy for separation, preconcentration of morin prior to its spectrophotometric determination. According to the literature survey, SUPRAS-AA-LLME method was not used for the separation and preconcentration of morin in fruit and beverage samples.

The main objective of this paper is the development of a new, simple, effective, and green SUPRAS-based AA-LLME for the extraction and preconcentration of morin in fruit and beverage samples. Application of an alkanol-based SUPRAS (1-dodecanol/THF) in improves the performance of the microextraction procedure reducing the time of analysis, considerably.

Experimental

Chemicals and Reagents

Analytical grade chemicals including 1-hexanol ($\geq 99\%$, $d = 0.814$ g mL⁻¹), 1-dodecanol ($\geq 98.0\%$, $d = 0.83$ g cm⁻³), 1-decanol ($\geq 99.0\%$, $d = 0.80$ g cm⁻³), 1-tetradecanol ($\geq 97\%$, $d = 0.823$ g cm⁻¹, Sigma), and tetrahydrofuran (Carlo Erba, THF) were used to prepare alkanol-based SUPRASs. Ultrapure water was prepared by Milli-Q water purification system (Millipore, Bedford, MA, USA). Stock solution (1000 mg L⁻¹) of Al(III) ion was prepared from Al(NO₃)₃ salt (Sigma, St Louis, MO, USA) in water and stored at 4 °C in a refrigerator. A stock solution of morinhydrate was prepared in ethanol at a concentration of 1000 mg L⁻¹ (Carlo Erba, Milan, Italy) and stored in dark. The calibration solutions were freshly prepared by sequential dilution of the stock solutions. A 5% (w/v) of KCl solution was prepared by dissolving 5.0 g of KCl (Sigma) in 100 mL deionized water. Borate, acetate, phthalate, and citrate buffer solutions were used to adjust solutions pH. To minimize all possible contamination of glassware, a diluted HNO₃ solution was used for washing glassware and finally rinsed with distilled water.

Instruments

A spectrophotometer (Shimadzu 1800 model, Kyoto, Japan) controlled by a HP model computer and equipped with a 500 μL quartz cell was used to obtain all analytical measurements. A pH meter (692, Herisau, Switzerland) was used to adjust the pH of the sample solution. Frequency and temperature-controlled ultrasonic water bath (Kudos, Shanghai, China) was employed in sample preparation and SUPRASs formation. A centrifuge (320R

model, Universal Hettich, London, UK) was used for phase separation.

Real Samples

Different fresh fruits and beverage samples, such as kiwi, strawberry, apple, blueberry, orange, pineapple, red wine, cherry juice, apple juice, tangerine juice, herbal tea, and grape fruit juice samples, were obtained from local market in Sivas, Turkey. Since morin is a flavone that can degrade depending on factors such as pH, temperature, and light, ultrasound-assisted sample preparation was applied as follows (Altunay et al. 2019). For degassing of red wine (10 mL), 1.0 mL 0.5% (v/v) of 1-octanol was added to the sample and vortexed for 2 min. Beverages (5 mL) and fruit (3 g) were carefully poured into test tubes and then 2 mL 0.01 mol L^{-1} of ascorbic acid was added into the mixture in order to ensure the stability of the morin. Following this, 24 mL of acidic methanol and 6 mL of 0.2 mol L^{-1} trifluoroacetic acid were added to the resulting mixture, respectively. The test tubes were placed in an ultrasonic bath and sonicated for 15 min at 40 °C. After centrifugation (4000 rpm for 5 min), the final solution was filtered through a 0.45 μm pore size membrane.

Preparation of Alkanol-Based SUPRAS

Alkanol-based SUPRASs were prepared according to a previously reported method (Moradi et al. 2015). Briefly, 500 μL of each alcohol (1-decanol, 1-hexanol, 1-dodecanol, and 1-tetradecanol) were mixed with 200 μL of THF, independently, and the resulting mixture was vortexed for 5 min at room temperature. After the formation of the alkanol-based SUPRASs, the solution was centrifuged. Subsequently, the less density SUPRASs were removed and used in the next experiments. The composition, mole ratio, and abbreviations of the prepared alkanol-based SUPRAS are given in Table 1.

Table 1 Composition, molar ratio, and abbreviations of the prepared alkanol-based SUPRAS

Abbreviations	Composition		Molar ratio	Recovery (%)
SUPRAS-1	1-Decanol	THF	1:2	61.7
SUPRAS-2	1-Hexanol	THF	1:2	81.4
SUPRAS-3	1-Dodecanol	THF	1:1	85.7
			1:2	90.1
			1:3	95.9
			1:4	84.7
SUPRAS-4	1-Tetradecanol	THF	1:2	76.2

Alkanol-Based SUPRAS Liquid–Liquid Microextraction

A 5.0 mL of the sample solution containing 100 μg L^{-1} of morin was placed into a 15-mL centrifuge tube. Then, 350 μL of 5 mg L^{-1} Al(III) solution was added to the sample solution adjusted at pH 4.5. Then, 500 μL of 1-dodecanol/THF SUPRAS (at a molar ratio of 1:3) containing 2.0% KCl (*w/v*) solution was added into the obtained mixture. The resulting mixture was sucked into a 10-mL glass syringe and then injected rapidly through the syringe needle for eight times. After this step, a cloudy mixture, which means the formation of fine droplets of the SUPRAS, was obtained. Then, in order to accelerate the extraction, the centrifuge tubes were placed in an ice bath for 10 min. At this stage, the solidified SUPRAS containing Al-morin complex was collected on the top of the solution and it was carefully transferred to another centrifuge tube, and melted at room temperature. Finally, morin determination was performed by a spectrophotometer at 348 nm (see Figure S1).

Result and Discussion

Effect of pH

In extraction procedures, the analyte molecules could be directed towards the ionization or molecular forms, through pH adjustment. In order for easier extraction of the analyte from aqueous samples, it must be directed towards neutral forms. In this method, formation of a complex between morin and Al(III) ions is affected by pH of the microextraction media. Therefore, the recovery of morin was investigated within the pH range of 3–9 (see Fig. 1a) by using 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 μL of SUPRAS mixture of (1:3) molar ratio (1-dodecanol-THF), and 2% (w/v) KCl. Recovery of morin was increased by increasing pH values and it was reached to quantitative value at pH 4.5 and after pH 5.0 it was decreased. The reason of decrease in recovery of morin at high pH values may be due to hydrolysis of either Al(III) with formation of metal hydroxides or decrease in stabilization constant of morin with increasing pH values. Therefore, the pH 4.5 obtained using the acetate buffer solution was chosen as optimum for the next steps.

Effect of Al(III) Amount

Chelate formation is an important factor for spectrophotometric determination of morin in SUPRAS-AA-LLME method. The obtained results are given in Fig. 1b. Recovery of morin was found 55% without Al(III) ions. When Al(III) amount increased, recovery of morin was increased and
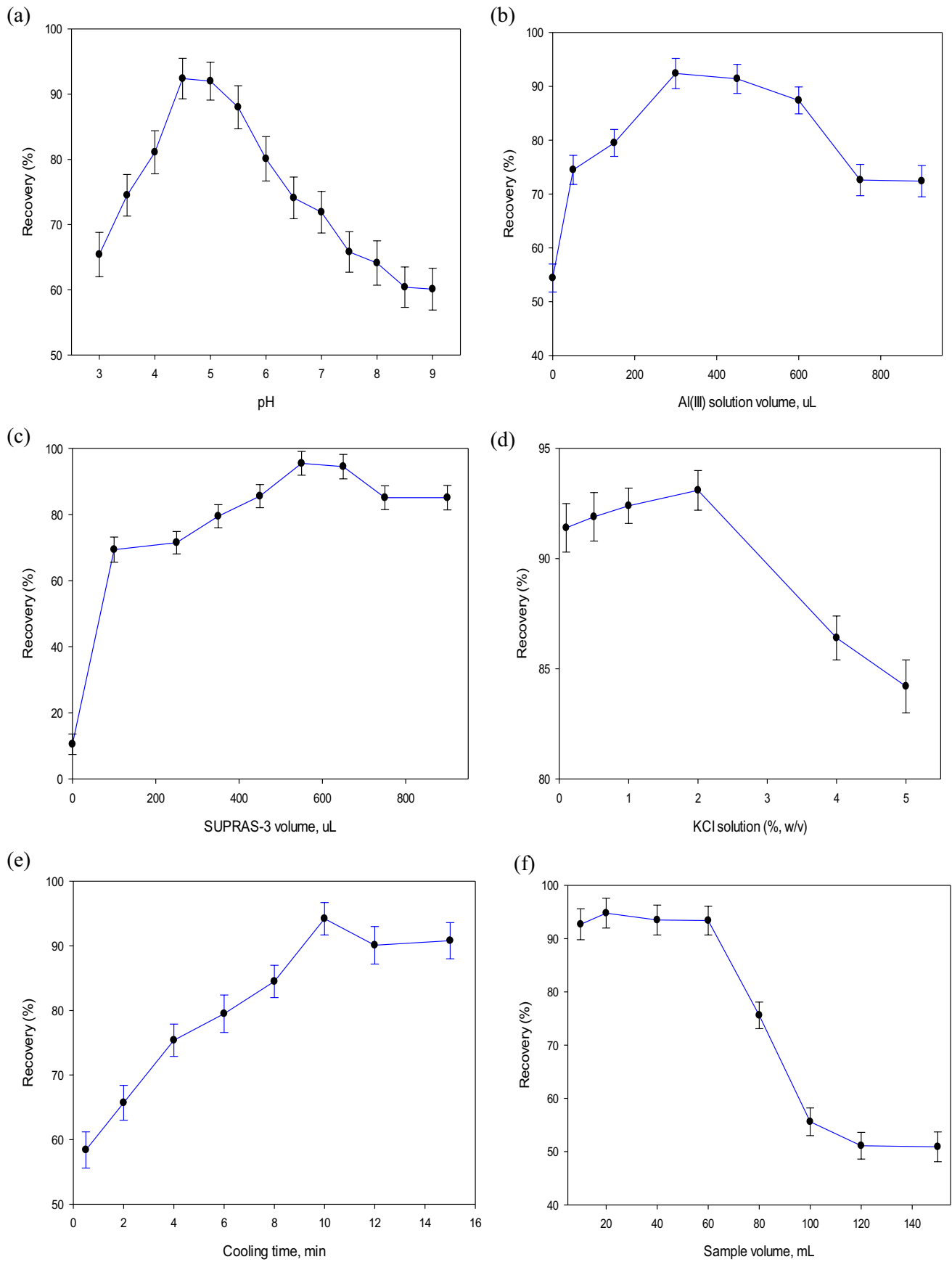
◄**Fig. 1 a–f** The results of the optimization studies. The microextraction conditions were as follows: 5.0 mL aqueous solution containing morin; pH, 4.5; 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution; 550 μL of SUPRAS-3; 2% (w/v) KCl; 10 min cooling time, and 60 mL sample volume

reached to quantitative value by using 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 μL of SUPRAS mixture of (1:3) molar ratio (1-dodecanol-THF), 2% (w/v) KCl, and 10 min cooling time at pH 4.5. Stable complex formation of morin with Al(III) ions was increased extraction efficiency of analyte to SUPRAS phase from aqueous solution. When using high amount of Al(III) ions, recoveries were decreased because of increasing reagent blank in sample solution. Therefore, 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution was chosen as optimum values for Al(III) solution for the next steps.

Effect of SUPRAS Type and its Composition

In SUPRAS-AA-LLME method, selection of SUPRAS type and are important factors for both effective phase separation and quantitative analytical results. Alkanol containing SUPRAS provides hydrogen bonding and dispersion interactions for morin in sample solution. Four different alkanol-based SUPRASs were prepared using combinations of THF and 1-decanol, 1-hexanol, 1-dodecanol, and 1-tetradecanol, separately (see Table 1). Quantitative recoveries of morin were found by using SUPRAS-3 (mixture of 1-dodecanol and THF, 1:3 molar ratio) as extraction solvent. Recoveries of morin were found in the range of 61.7–85.7% by using other alkanol-based SUPRAS composition. The SUPRAS-3 volume was also an important factor for extraction efficiency and formation of microspheres. Therefore, the effect of SUPRAS-3 volume on recovery of morin was investigated in the range of 0.0–900 μL. Quantitative recoveries of morin were performed by using 550 μL SUPRAS-3 (see Fig. 1c). Therefore, 550 μL SUPRAS-3 (mixture of 1-dodecanol and THF, 1:3 molar ratio) was chosen as optimum for the next steps.

Effect of Ionic Strength

Due to the fact that ionic salts have the highest solubility in water, addition of them to the solution facilitates the analyte extraction migration into the extraction solvent. Accordingly, easy phase separation and quantitative recovery can be achieved. In order to study the effect of ionic strength on the performance of the present method, different amount of KCl solutions (0.1–5%) was added to model solutions and present method was applied by using 100 μg L^{-1} morin, 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 μL of SUPRAS

mixture of (1:3) molar ratio (1-dodecanol-THF), and 10 min cooling time at pH 4.5. From the results in Fig. 1d, recoveries of morin were found quantitative until addition of 2% KCl solution. When added to 5% KCl in sample solution, the recoveries of morin were decreased to 85% because of causing matrix effects of high amount of salt. Therefore, 2% KCl solution was chosen as optimum for the next steps.

Effect of Cooling Time

The phase containing the analyte and collected on the aqueous solution must be allowed to solidify in order to separate it from the sample solution. If a suitable solidified phase cannot be obtained, phase separation will not be achieved and non-quantitative recovery can be obtained. For these reasons, effect of cooling time on the recovery of morin was investigated in the time ranges from 1 to 15 min. Recovery values were found below 60% without cooling the sample solution. In order to increase extraction efficiency of analyte, model solution was cooled in ice bath in the range of 1–15 min using 100 μg L^{-1} morin, 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 μL of SUPRAS mixture of (1:3) molar ratio (1-dodecanol-THF) at pH 4.5 (see Fig. 1e). Model solution was cooled in ice bath for 10 min to accelerate the extraction of the morin-Al(III) complex into the microspheres. Solidified SUPRAS phase containing Al(III)-morin complex was collected on the upper surface of the tubes. The solidified SUPRAS phase was carefully transferred to another test tube and dissolved rapidly at room temperature.

Effect of Sample Volume

In order to obtain high preconcentration factor (PF), sample volume was a very important factor. PF was calculated by dividing the sample volume to the final collected volume. Different sample solutions in the range of 10–150 mL containing 50 μg L^{-1} morin were prepared and then subjected to the developed method by using 300 μL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 μL of SUPRAS mixture of (1:3) molar ratio (1-dodecanol-THF), 10 min cooling time at pH 4.5 (see Fig. 1e). It was shown that the recoveries of morin were found quantitative till 60 mL and then decreased at 70–150 mL sample volume. PF, which was calculated as divided of highest sample solution volume (60 mL) to minimum final solution volume (0.5 mL), was found 120.

Matrix Effects

The tolerance limit of interference ions was defined as ion concentration causes more than ± 5% change in the analytical signal. Levels of interfering ions were very important for the selectivity of the method. Different

Table 2 The matrix effect on preconcentration and determination of 100 µg L^{-1} morin ($N=3$)

Interference ions	Tolerance limit	Recovery (%)	RSD (%)
Na(I)	2000	98.4	2.3
Ca(II)	2000	97.1	2.0
CO$_3$(II)	2000	98.5	2.5
Tartaric acid	1500	98.0	2.4
Ascorbic acid	1500	97.8	2.3
SO$_4$(II)	1500	97.5	2.1
Nicotinamide	1500	98.6	2.0
Apigenin	1000	98.6	2.1
Caffeine	500	98.2	2.6
Mn(II)	500	97.1	2.2
Cu(II)	500	96.4	2.3
Citric acid	250	96.2	2.1
Zn(II)	250	96.2	2.5
Catechin	250	95.7	2.4
Fe(III)	250	95.8	2.3
Caffeine	100	95.5	2.3
Rutin	100	95.3	2.4
Quercetin	100	95.1	2.2
Kaempferol	100	95.4	2.1

Table 3 Analytical features of the present method

Parameters	Values obtained
Calibration equation	A $= 1.34 \times 10^{-3}$ [morin, µg L^{-1}] $+ 5.07 \times 10^{-4}$
Regression coefficient (r^2)	0.9982
Linear range (µg L^{-1})	10–800
LOD ($3 \times S_{blank}/m$, µg L^{-1})	3.5
LOQ ($10 \times S_{blank}/m$, µg L^{-1})	10
RSD% (n:10, 50 µg L^{-1})	3.1
Preconcentration factor	120
Enhancement factor	95
Measurement wavelength, nm	348

µg L^{-1}] $+ 5.07 \times 10^{-4}$ after the developed method. The enhancement factor (EF), calculated from the slope ratio of the calibration graph with and without the SUPRAS-AA-LLME, was found to be 95. Comprehensive data are given in Table 3.

Validation and Applications of the SUPRAS-AA-LLME Method

Precision and accuracy of the method were examined for real sample solutions. The precision of the present method was investigated as RSD and it was found separately for repeatability (n: 3 in the same day) and reproducibility (n: 3×3 in three consecutive days). For the quality control, kiwi and apple juice were used as reference for fruit and beverage samples. The data of the study are given in Table 4. The RSD values were found lower than 4% which confirms the acceptable precision of the method. Accuracy of the method was confirmed with standard addition. In the spiked levels of 10–50 µg kg^{-1} for fruit samples and 100–200 µg L^{-1} for beverage samples, recovery values were found quantitative (95–102%) and RSD values were found lower than 3%. Overall, the results achieved in the recovery and precision confirm that the method has concentrated and purified the desired analyte from the complex matrix of the selected sample with high accuracy and precision and confirms the validity of the method. Comprehensive data are given in Table 5.

The SUPRAS-AA-LLME method was applied on fruit and beverage samples including kiwi, strawberry, apple, blueberry, orange, pineapple, red wine, cherry juice, apple juice, tangerine juice, herbal tea, and grape fruit juice samples. The data obtained are given in Table 5. All sample solutions were diluted 100-fold in order to decline the morin concentration in the linear working area. The obtained results for morin in analyzed fruit and beverage samples were acceptable for the human consumption. Analyzed samples can make a significant contribution to morin intake.

levels of possible interfering ions were added to the model solutions containing 100 µg L^{-1} morin and then the presented method was applied. As can be seen from the results in Table 2, there is no significant effect of interference ions on the recovery of morin under the optimized experimental conditions (300 µL of 10^{-3} mmol L^{-1} of Al(III) solution, 550 µL of SUPRAS mixture of (1:3) molar ratio (1-dodecanol-THF), 10 min cooling time, and pH 4.5 by using acetate buffer solution). It can be said that SUPRAS-AA-LLME method has high selectivity, and tolerance limit, quantitative recovery (95.1–98.6%), and low relative standard deviation (RSD) values (2.1–2.6%).

Analytical Figure of Merits

Detection limit (LOD) and quantification limit (LOQ) for the SUPRAS-AA-LLME method were calculated from the equations of 3 s/m and 10 s/m, where s is standard deviation of the eleven-reagent blank solution and m is slope of the calibration curve. LOD and LOQ were found at 3.5 and 10 µg L^{-1} for water samples, 4.1 and 14 µg kg^{-1} for solid samples, respectively. RSD of the present method was found to be 3.1% from the analysis of ten replicates of 10 mL sample solution containing 100 µg L^{-1} morin. The linearity was achieved in the range of 10–800 µg L^{-1} ($r^2 = 0.9982$), with a linear calibration equation A $= 1.34 \times 10^{-3}$ [morin,

Table 4 The accuracy and precision of the present method for two quality control samples after spiking

Samples	Spiking (µg L^{-1})	Intra-day (*n*: 3 in same day)			Inter-day (*n*: 3 × 3 in three consecutive days)		
		Found (µg L^{-1})	RSD (%)	Recovery (%)	Found (µg L^{-1})	RSD (%)	Recovery (%)
Kiwi	25	24.1	3.1	96.4	23.4	3.9	93.6
	300	305.8	2.9	101.9	307.9	3.5	102.6
	600	586.1	2.7	97.7	571.8	3.1	95.3
Apple juice	25	26.3	3.6	105.2	23.9	4.2	95.6
	300	288.5	3.3	96.2	282.4	3.7	94.1
	600	612.4	3.0	102.1	624.5	3.4	104.1

Table 5 The analysis results of extraction of morin in fruit and beverage samples by using the present method (*n*:5)

Matrix type	Spiked	Found	RSD (%)	Recovery (%)
Fruit samples (µg kg^{-1})				
Kiwi	-	81.4	2.1	-
	10	91.0	2.3	96.0
	50	130.2	2.4	97.5
Strawberry	-	179.2	2.6	-
	10	188.9	2.8	97.0
	50	227.8	2.8	97.2
Apple	-	231.8	2.0	-
	10	241.3	2.4	95.0
	50	280.2	2.5	96.8
Blueberry	-	192.1	2.2	-
	10	201.8	2.5	97.0
	50	241.5	2.6	98.7
Orange	-	262.7	1.9	-
	10	272.2	2.2	95.0
	50	311.4	2.4	97.4
Pineapple	-	114.3	2.2	-
	10	124.5	2.3	102.0
	50	165.1	2.6	101.5
Beverage samples (µg L^{-1})				
Red wine (sample 1)	-	125.4	2.4	-
	100	221.1	2.5	95.7
	200	321.0	2.7	97.8
Red wine (sample 2)	-	110.2	2.5	-
	100	213.7	2.6	103.5
	200	314.4	2.8	102.1
Cherry juice	-	75.6	2.1	-
	100	172.5	2.3	96.9
	200	270.4	2.4	97.4
Apple juice	-	157.9	2.3	-
	100	260.6	2.5	102.7
	200	361.1	2.7	101.6
Tangerine juice	-	95.1	2.7	-
	100	192.5	2.8	97.4
	200	291.7	3.1	98.3
Herbal tea	-	146.8	2.8	-
	100	244.0	3.0	97.2
	200	344.0	3.2	98.6
Grapefruit juice	-	101.6	2.5	-
	100	204.9	2.7	103.3
	200	305.4	2.8	101.9

Table 6 Comparison of the present method with previously reported methods in the literature

Microextraction procedure	Detection technique	Matrix type	[a,b,c] Linear range	[a,b,c] LOD	RSD (%)	EF or PF	Refs
SBME-DES	HPLC–UV	Vegetable and fruit juice	[a]1–500	[a]2.6	3.5	36.1	Nia and Hadjmohammadi (2019)
HF-LPME	HPLC–UV	Fruit juice	[a]5–500	[a]1.5	7.2	293	Hadjmohammadi et al. (2013)
VA-ILME	UV–VIS	Food and beverages	[a]17.5–450	[a]5.3	1.9	50	Altunay et al. (2019)
S-SIL-MSPD	HPLC–DAD	Raw propolis samples	[c]0.09–47.26	[c]0.02	< 8.95	-	Wang et al. (2014)
-	SWV	Grape wine	[b]0.01–5	[b]0.0033	1.69	-	Yola et al. (2014)
DM-SPE	HPLC–UV	Fruit juices and vegetable	[a]2.7–500	[a]0.83	3.66	-	Sani et al. (2020)
DES-MD-SPE	HPLC–UV	Apple and grape juices, tea	[a]3–500	0.91	3.8	39.1	Majidi and Hadjmohammadi (2019)
SUPRAS-AA-LLME	UV–VIS	Fruit and beverage	[a]10–800	[a]3.5	3.1	120	Current study

[a]$\mu g\,L^{-1}$, [b]$\mu mol\,L^{-1}$, [c]$mg\,L^{-1}$

SBME-DES, solvent bar microextraction based on a deep eutectic solvent; *HPLC–UV*, high-performance liquid-chromatography ultraviolet detection; *HF-LPME*, hollow fiber liquid-phase microextraction; *VA-ILME*, vortex-assisted ionic liquid-based microextraction; *S-SIL-MSPD*, silica-supported ionic liquid-matrix solid-phase dispersion; *SWV*, square wave voltammetry; *DM-SPE*, dispersive magnetic solid-phase extraction; *DES-MD-SPE*, alcohol-based deep eutectic based on magnetic dispersive solid-phase extraction

Conclusions

Simple, rapid, effective, and green SUPRAS-based AA-LLME method was developed for separation, preconcentration, and spectrophotometric determination of morin in fruit and beverage samples. Four different alkanol-based SUPRASs were prepared for the extraction of Al(III)-morin complex from aqueous solution. The accuracy of the present method was confirmed with standard addition method. RSD values were calculated for intra- and inter-day precision and they were found below 4%. The present method has some advantages such as sensitivity, selectivity, and high tolerance limit, short extraction time, low cost, and easy for separation and preconcentration of morin. The comparisons of the SUPRAS-AA-LLME method with literature values are given in Table 6. In comparison to the other methods, the SUPRAS-AA-LLME method has the advantages of shorter extraction time, simplicity, and applicability in routine analysis laboratories. Moreover, low detection, low RSD, high PF/EF, and wide linear working area were observed in the present method according to literature values. Very complex fruit, beverage, and food samples can be analyzed with the present SUPRAS-AA-LLME method at $\mu g\,L^{-1}$ levels with respect to morin-containing flavonoid samples.

Declarations

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