



A Simple and Cheap Ultrasound-Assisted Microextraction Procedure For Extraction of Tartrazine in Soft Drinks and Foodstuff

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Abstract. In this study, a simple and cheap ultrasound-assisted ionic liquid-based floating organic droplets microextraction (UA-IL-FODME) has been proposed for spectrophotometric determination of synthetic food dye (tartrazine) in soft drinks and food samples. 1-Octyl-3-methylimidazolium tetrafluoroborate [C8MIM][BF₄] and 1-octanol were used as the extraction solvent and dispersant solvent, respectively. The method is based on extracting the tartrazine to the ionic phase with the help of ultrasonic effect at pH 5.5. Some experimental variables (pH, ionic liquid amount, type and volume of dispersive solvent, and ultrasonic conditions) were studied and optimized in detail. In optimum conditions, some analytical parameters of the method were as follows. Operating range, limit of detection, preconcentration factor, recovery % and RSD % values were 10-700 µg L⁻¹, 3.2 µg L⁻¹, 75, 94.7-104.7% and 2.7%, respectively. Following comprehensive validation studies, the recommended method was successfully applied to the extravasation and determination of tartrazine in soft drinks and foodstuff.

Keywords: Floating organic droplets, Ionic liquid, Ultrasound, Tartrazine, Soft drinks, Foodstuff.

Alkolsüz İçecekler ve Gıda Ürünlerinde Tartrazinin Özütleme için Basit ve Ucuz Ultrason Destekli Mikroekstraksiyon Prosedürü

Özet. Bu çalışmada, basit ve ucuz ultrason destekli iyonik sıvı bazlı yüzer organik damlacıklar mikroekstraksiyonu (UA-IL-FODME), sentetik yiyecek boyalarının (tartrazin), alkolsüz içeceklerde ve gıda ürünlerinde spektrofotometrik olarak belirlenmesi için önerilmiştir. 1-Oktil-3-metilimidazolium tetrafloroborat [C8MIM] [BF₄] ve 1-oktanol sırasıyla ekstraksiyon çözücü ve dağıtıcı çözücü olarak kullanılmıştır. Yöntem, pH 5.5'te tartrazin 'in iyonik faza ultrasonik etki yardımıyla özütleme dayanır. Bazı deneysel değişkenler (pH, iyonik sıvı miktarı, dispersiv çözücü çeşidi ve hacmi ve ultrasonik koşullar) çalışıldı ve ayrıntılı olarak optimize edildi. Optimum koşullarda, yöntemin bazı analitik parametreleri aşağıda özetlenmiştir. Çalışma aralığı, seçme sınırı, ön konsantrasyon faktörü, geri kazanma yüzdesi ve %BBS değerleri sırasıyla 10-700 µg L⁻¹, 3.2 µg L⁻¹, 75, % 94.7-104.7 ve % 2.7 idi. Kapsamlı validasyon çalışmalarının ardından, önerilen yöntem, alkolsüz içecekler ve gıda maddelerinde tartrazin mikroekstraksiyonu ve tayinine başarıyla uygulanmıştır.

Anahtar Kelimeler: Yüzen organik damlacıklar, İyonik sıvı, Ultrason, Tartrazin, Alkolsüz içecekler, Gıda ürünleri.

1. INTRODUCTION

In the world, food production and consumption are increasing due to population growth. Food additives should be used to prevent food spoilage during transportation and storage. [1]. Food dyes are defined by the International Food Codex Commission as additives to regulate the color of the dish. [2]. Nowadays, for technological reasons, it is suggested that foods should be colored [3]. Synthetic colorants are substances which can be produced by chemical synthesis. Synthetic colorants provide superiority in terms of color strengths, color ranges, stability, ease of use and price compatibility according to natural colorants. [4]. Tartrazine is water soluble synthetic food dye and its code is E102. Food additives are widely used for different purposes, including preservation, coloring and taste. However, some food additives are prohibited due to their toxicity [5]. Among the five azo dyes, Amaranth, Allura Red, New Coccine and Tartrazine (initially 10 ppm) lead to dose-related DNA fragmentation in the colon [6]. Tartrazine can cause allergic and asthma problems in delicate people. The analytical control of these compounds is important for the food industry due to their toxicity and carcinogenicity [7]. Therefore, simple, inexpensive and fast analytical methods are needed to determine synthetic dyes in food. Analytical methods for the analysis of synthetic colorants in food and beverages have been reported in literature. These methods are based on the basis of the thin layer chromatography (TLC) [8], high performance liquid chromatography (HPLC) with diode array detection (DAD) and ion-trap time-of-flight mass spectrometry (IT-TOF/MS) [9], spectrophotometry [10], electrochemical sensor [11], high performance liquid chromatography (HPLC)-diode array detector (DAD)-electrospray mass spectrometry (ESI-MS) [12]. It is also necessary to minimize possible matrix effects when analyzing at low levels. Therefore, different extraction methods such as solid phase extraction (SPE) [13], liquid-liquid extraction (LLE) [14], cloud point extraction (CPE) [15], molecularly imprinted solid-phase extraction (MISPE) [16], ultrasound-assisted extraction (UAE) [17-19] and ionic liquid based liquid phase microextraction (IL-

LPME) [20-22] were applied before determination step. In addition to these extraction methods, in the recent years, extraction methods using ionic liquid (IL) have become popular. Some of ILs properties are low toxicity, high vapor pressure, biodegradable and high hydrophobicity.

The purpose of this study is to develop a simple and cheap analytical method for the determination and extraction of tartrazine in soft drinks and foodstuff. In this context, the ultrasonic-assisted ionic liquid-based floating organic droplets microextraction procedure (UA-IL-FODME) was developed and UV-VIS spectrophotometry was used in the determination step. Factors affecting the extraction of tartrazine were investigated in detail. The proposed method can be applied for determination of tartrazine in soft drinks and foodstuff. After routine applications, the results shown that the proposed method is suitable for the extraction and determination of tartrazine in different food samples.

2. MATERIALS AND METHODS

2.1. Apparatus

In the study, tartrazine content in selected samples was determined at 425 nm using Shimadzu brand UV-VIS spectrophotometry (UV-1800 PC model, Kyoto, Japan). Ultrapure water with resistivity of 18.2 M Ω cm was obtained by a Milli-Q water purification system (Millipore Corp., USA). Extraction of tartrazine from sample solution was achieved by a universal hettich brand centrifuge (Hettich, London, England). The pH of samples solution was adjusted using a digital pH meter (Sartorius Docu-model, North America). An ultrasonic bath (UCS-10 model, Seoul, Korea) was used for both sample preparation and the formation of microsphere of ionic liquid.

2.2. Chemical and Reagents

The reagents used were of analytical purity, and were purchased from Sigma (St. Louis, MO, USA) and Merck (Darmstadt, Germany). The stock solutions of tartrazine (Sigma) was prepared in water. Working standards were prepared by dilution of the stock solution. 1-Octyl-3-

methylimidazolium tetrafluoroborate ([C8MIM][BF₄]) (Sigma) was used as extraction solvent. Acetone (Merck), 1-heptanol (Merck), 1-octanol (Merck), ethanol (Sigma), 2-propanol (Sigma), and methanol (Merck) were tested as dispersive solvents. pH 5.5 of acetate buffer solution (0.1 M) was prepared by mixing an appropriate amount of sodium acetate and acetic acid in water. Before the experiment, all materials were washed in dilute nitric acid, followed by rinsing three times with distilled water, respectively.

2.3. Sample collection and preparation

Soft drinks and foodstuff were collected randomly from the local markets in Sivas, Turkey. Ultrasonic-assisted sample preparation step was carried out as follows: First, 50 mL centrifuge tubes were taken, and then 2 g of foodstuff and 3 mL of soft drinks were added to the tubes. Final volume of tubes was diluted to 50 mL, were placed in ultrasonic bath, and then sonicated for 15 min at 30 °C. The resulting mixture was filtered through the membrane filter after centrifugation at 4000 rpm for 5 min. The same experimental steps were performed to the blank sample. The proposed method was applied to 1.0 mL of the prepared samples.

2.4. UA-IL-FODME procedure

The UA-IL-FODME procedure was performed in 15-mL centrifuge tubes. First, an aliquot of 1.0 mL sample solution containing 25 µg L⁻¹ of tartrazine was added to the tubes. Then the pH of the sample solution was adjusted to pH 5.5 with acetate buffer. To ensure the extraction of tartrazine from the sample solution, 400 µL of [C8MIM][BF₄] (extraction solvent) and 300 µL of 1-octanol (dispersive solvent) were added rapidly with a micro syringe into the sample solution. The tubes were sonicated for 5 min at 45 °C in the ultrasonic bath to form the microspheres of the [C8MIM][BF₄]. The tubes were centrifuged at 4000 rpm for 2 min, and then were stored in an ice bath to facilitate phase separation. At this stage, the dispersive solvent (1-octanol) was solidified within 2 min. After decantation, the remaining phase was

completed to 500 µL using ethanol. Finally, the amount of tartrazine was determined at 425 nm by UV-Vis spectrophotometry. A blank solution was also carried out using the same experimental steps without tartrazine.

3. RESULTS AND DISCUSSION

3.1. Selection of working wavelength

The most important step of the experimental studies using UV-Vis spectrophotometry is the selection of the measurement wavelength. Because all the experimental measurements were performed at the selected wavelength. If the correct wavelength is not selected, all experimental results are affected. Therefore, the following experimental steps were taken to determine the appropriate wavelength. First, only the tartrazine in the aqueous solution was obtained at the spectrum. Second, the spectrum of tartrazine in the presence of other chemicals was taken. The results were given in Figure 1. As the results show, the tartrazine spectrum gave a weak spectrum at 435 nm, while in the presence of IL a sharp spectrum was obtained at 425 nm. In addition, the absorbance of the obtained spectrum shows a linear increase with the concentration of tartrazine. These reasons were chosen as the appropriate wavelength of 425 nm for optimization and analysis.

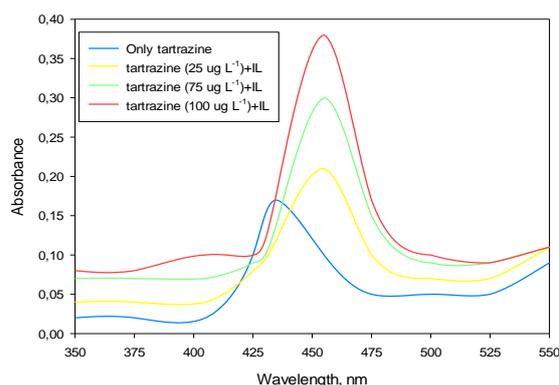


Figure 1. Absorbance spectra obtained in selected chemical conditions.

3.2. Effect of pH

Electrostatic interactions between chemical species vary depending on the pH of the aqueous solution. In the extraction experiments, the interaction between the analyte and the selected chemical

medium should be high. Depending on the interaction, the target analyte can be easily extracted from the aqueous solution. For a clearer view of this, the effect of the pH of the aqueous solution on the absorbance of tartrazine was investigated in the range of pH 3-9. As shown in Figure 2, the absorbance of tartrazine increased in the range of pH 3 to 5.5, and there was a decrease in absorbance at higher pH values. The reason for the decrease in absorbance at high pH is due to the loss of hydrogen from tartrazine. So, pH 5.5 of acetate buffer was selected as the optimum pH for higher absorbance and easy phase separation.

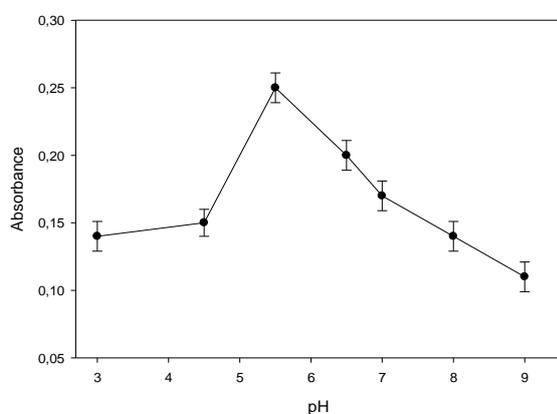


Figure 2. Effect of pH on absorbance of tartarazine

3.3. Effect of [C8MIM][BF₄] amount

In these methods, the selection of the appropriate extraction solvent is necessary to good extraction. The following specifications should be taken into account when selecting the extraction solvent. (I) The selected solvent must be green. (II) A small amount of the extraction solvent should be sufficient for extraction. (III) the extraction solvent should be selective for the analyte. (IV) The extraction time should be short. Taking these properties into consideration, the ionic liquids (IL) such as [C8MIM][BF₄] used in many fields were chosen as extraction solvents. The [C8MIM][BF₄] must be in sufficient volume in the final volume in order to ensure the extraction. Therefore, the effect of the amount of [C8MIM][BF₄] on the absorbance of the tartrazine was investigated in the range of 0-800 μ L. As shown in Figure 3, the extraction depend on the amount of [C8MIM][BF₄]. Phase separation was not achieved in the absence of

[C8MIM][BF₄], and maximum absorbance was obtained when the [C8MIM][BF₄] amount was 400 μ L. So, 400 μ L of [C8MIM][BF₄] was selected as the optimum value for higher absorbance and easy phase separation.

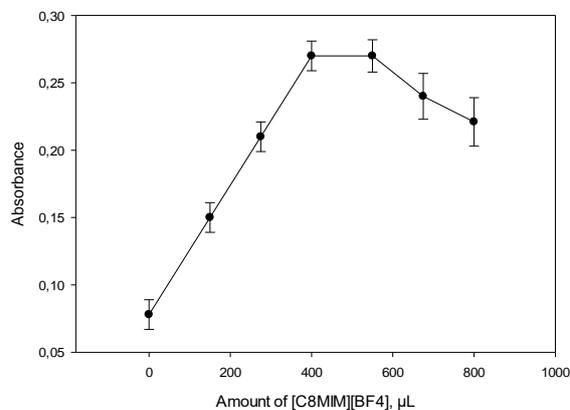


Figure 3. Effect of [C8MIM][BF₄] amount on absorbance of tartarazine

3.4. The effect of the type and volume of dispersive solvent

The main purpose of the dispersive solvent is that the extraction solvent provides microsphere formation. The dispersive solvent should also be dispersible between the ionic liquid and the aqueous phase. For the selection of dispersive solvents, different solvents (acetone, 1-heptanol, 1-octanol, ethanol, 2-propanol, and methanol) preliminary tests were made, and the best signals and phase separation were obtained in the presence of 1-octanol. So, 1-octanol was chosen as the dispersive solvent. The effect of the amount of this dispersive solvent on the absorbance of tartrazine was investigated in the range of 0-600 μ L. The results were given in Figure 4.

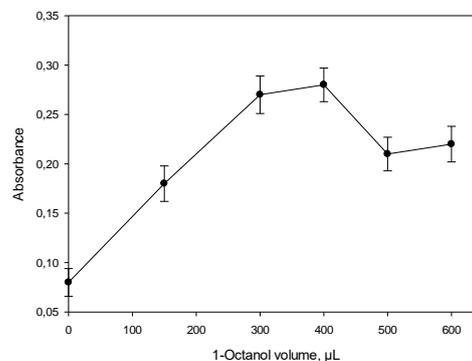


Figure 4. Effect of 1-octanol volume on absorbance of tartarazine

Quantitative results could not be obtained when dispersive solvent volume was low. The reason for this is that there is not enough dispersive solvent in the medium to disperse the [C8MIM][BF₄]. The highest absorbance values were obtained in the range of 300-400 μ L of 1-octanol. At higher 1-octanol volumes, there was a partial reduction in absorbance. So, 300 μ L of 1-octanol was selected as the optimum value for higher absorbance and easy phase separation.

3.5. Effect of ultrasonication time

Ultrasonication is an important variable that accelerates phase separation. The ultrasound-induced cavitation makes the ionic liquid molecules in the aqueous phase move faster. Selection of appropriate ultrasonic time is essential for extraction. The effect of ultrasonic time on the absorbance of the tartrazine was investigated in the range of 1-20 min. As shown in Figure 5, quantitative absorbances were obtained in a 5 min ultrasound. In addition, over 10 min of ultrasound absorbance decreased. In later studies, 5 min of ultrasonication time was selected as the optimum value for higher absorbance and easy phase separation.

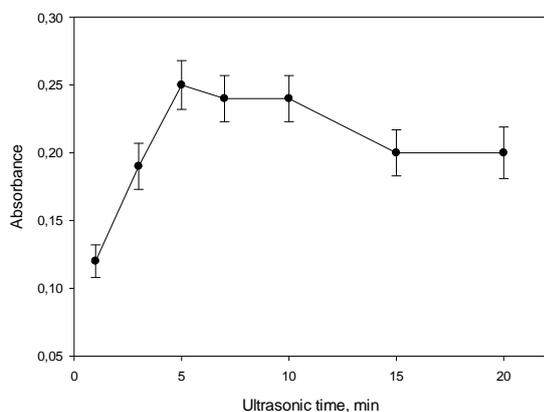


Figure 5. Effect of ultrasonic time on absorbance of tartrazine

3.6. Effect of temperature

Studies have been reported to provide phase separation at room temperature for ionic liquids. Additional experimental steps are implemented to increase the phase separation of ionic liquid. Some of them are vortexes, heating, and ultrasonic effect,

or a combination thereof. In this study, the heating effect is used to accelerate the phase separation of ionic fluid. And the effect of the working temperature on the absorbance of the tartrazine was investigated from room temperature to 60°C. The results were given in Figure 6. The highest absorbance was obtained at 45°C. The reason for the decrease in absorbance at high temperatures is the decrease in the effectiveness of the ionic liquid and dispersive solvent mixture. So, temperature (45°C) was selected as the optimum value for higher absorbance and easy phase separation.

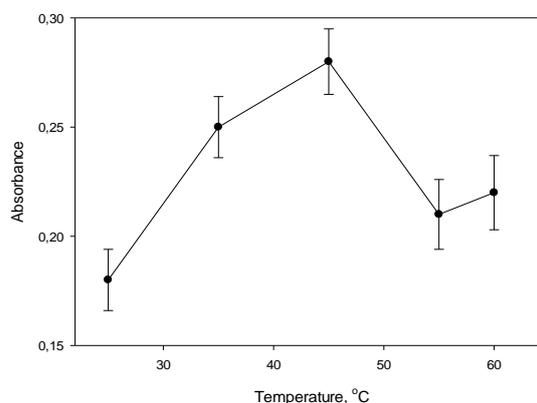


Figure 6. Effect of temperature on absorbance of tartrazine

3.7. Selectivity study

The selectivity of the analyte method is expressed as the interest of the selected chemical medium to the analyte in the sample medium. The higher the selectivity, the less analytical method has less interference. In general, experimental studies are performed with model solutions while developing a chemical method. The ability of the method developed when the real example is studied is not known. For this reason, it is necessary to carry out a selection study before the analysis of the real samples. These studies were carried out as follows. First, foreign ions at different proportions were added to the model solutions, and then the ability of the proposed method was tested in the presence of foreign ions by applying the proposed method. If an ion causes a $\pm 5\%$ change in the absorbance of the analyte, the ion is defined as an interference ion. In addition, the tolerance limits for the corresponding ion were determined by the ratio of the concentration caused by the interference to the

initial amounts of tartrazine. The result of the study was given in Table 1. The results indicate no significant interference effect. Second, the analytical properties of the method were determined by studies on matrix matched solutions.

The impact of all possible initiatives was reflected in all analytical data. Studies have shown that the selected chemical medium was highly selective for the tartrazine.

Table 1. Selectivity of the method in the presence of potential interfering species and tolerance limits

Interfering species	Tolerance limits	Recovery (%)	RSD (%)
Sn ²⁺	1000	94.7	2.1
Cd ²⁺	1000	96.4	2.4
K ⁺	1000	98.1	2.2
Co ²⁺	1000	95.3	2.1
Mg ²⁺	1000	96.2	2.0
Ca ²⁺	750	96.8	2.8
Tartaric acid	750	97.5	2.5
Ponceau 4R	750	96.5	2.6
Fe ³⁺	750	98.2	1.8
SO ₄ ²⁻	500	94.4	2.7
Allura red AC	500	95.9	2.5
Ascorbic acid	500	97.1	2.6
Al ³⁺	500	96.3	2.9
Brilliant Blue	250	96.5	2.5
Sunset yellow	250	93.4	2.4
Erythrosine	250	93.1	2.1
Carmoisine	100	92.4	2.8
Amaranth	100	92.5	2.5

3.8. Analytical performance

After both chemical variables and experimental conditions were optimized, the analytical parameters of the method were determined in selected chemical conditions. The working matrix was performed on matched solutions. The experimental steps were as follows. Different amounts of tartrazine were added to the prepared samples, and then the recommended method was applied. Analytical properties such as the working linear range, regression equation, detection limit (LOD), quantification limit (LOQ), preconcentration factor, sensitivity improvement

factor (SIF) and recovery were calculated from the results. The linear working range of the method was calculated as 10-700 µg L⁻¹. The SIF was calculated from the slope ratio of the calibration graphs before and after the UA-IL-FODME procedure, and was found as 127. The LOD and LOQ were expressed as the ratio of three and ten times the standard deviation of the blank samples to the slope of the calibration graph. The LOD and LOQ values were 3.2 µg L⁻¹ and 10 µg L⁻¹, respectively. Comprehensive analytical data was given in Table 2.

Table 2. Analytical parameters of the proposed method under optimum conditions

Parameters	For matrix-matched solutions
Regression equation	Abs.= 0.0018×[Tartrazine, µg L ⁻¹] + 0.00024
Correlation coefficient, r ²	0.9935
Working linear range, µg L ⁻¹	10-700
LOD, (µg L ⁻¹)	3.2
LOQ, (µg L ⁻¹)	10
Average RSD %	2.2
Average Recovery %	96.1
sensitivity improvement factor (SIF)	127
Pre-concentration factor (PF)	50

3.9. Validation study

The validation parameters (accuracy and precision) of the proposed method should be tested prior to the analysis of the real samples. Accuracy is expressed as the proximity of the experimental results to the actual accepting value. and the accuracy of the method was tested by recovery experiments. Precision refers to the proximity of the values found in an experiment. The precision of the method was assessed by the presence of relative standard deviation (RSDs%) value. The test of these parameters was evaluated with intra-day and inter-day studies. Both studies were tested for three different concentrations of tartarazine. Intra-day study, triplicate experimental study was carried out in one day for each concentration. In inter-day study, three repetitive studies were continued in three consecutive days. The RSD% values for

intra-day and inter-day study ranged between 1.8-3.5% and 2.2-3.8%, respectively. In addition, quantitative recoveries (95.4-103.2% for intra-day 93.3-105.2% for inter-day) were obtained for both studies.

3.10. Application

After all the analytical parameters of the method were tested, the applicability of the method was evaluated for the extraction and determination of taratizine from the soft drinks and foodstuff. Taking 1.0 mL of the prepared samples as described in Section 2.3, the recommended method was applied, and the amount of tartarazine in each sample was determined separately. Recovery experiments were also performed. Analytical results are given in Table 3.

Table 3. Analytical results of the proposed method

Sample	Tartarazine ($\mu\text{g L}^{-1}$)		Recovery %	RSD %
	Added	Found		
Syrup-preserved fruit	-	75.4	-	1.4
	100	170.7	95.3	1.7
	200	269.0	96.8	1.8
Carbonated drink-green	-	117.5	-	2.1
	100	219.7	102.2	2.4
	200	320.9	101.7	2.5
	-	321.0	-	1.8
Carbonated drink-orange	100	417.4	96.4	1.7
	200	516.6	97.8	1.9
Chocolate candy-green	-	166.0	-	1.7
	100	259.8	93.8	1.8
	200	358.2	96.1	2.1
Chocolate candy-yellow	-	245.1	-	1.8
	100	340.8	95.7	2.0
	200	442.9	98.9	2.1
	-	450.0	-	1.8
Lollipop	100	511.4	101.4	2.1
	200	652.0	101.0	2.2
	-	314.7	-	2.3
Icing sugar	100	414.7	96.6	2.1
	200	510.3	97.8	2.0

The amount of tartrazine ranged from 75.4-321 $\mu\text{g L}^{-1}$ for the soft drinks and ranged from 166 to 450 $\mu\text{g L}^{-1}$ for foodstuff. Furthermore, the RSD% and recovery values for soft drinks and foodstuff samples were 1.4-2.5%, 95.3-102.2% and 1.7-2.3%, 93.8-101.4%, respectively. In order to understand the positive aspects of the proposed

method in literature, the method used was compared analytically with the other methods reported. The analytical properties compared were the operating range, detection limit, preconcentration factor, RSD% and recovery. When the Table 4 was examined, it was understood that the proposed method has a wider working

range and a lower detection limit than other methods. According to other extraction methods, in this study, more environmentally friendly and cheap chemicals were used. In the determination step, the use of cheap and easy to use

spectrophotometer that can be found in almost any laboratory is alternative to expensive and complex techniques such as HPLC.

Table 4. Comparison of analytical performance of the proposed method with other methods.

Extraction	Detection technique	Linearity ($\mu\text{g L}^{-1}$)	Detection limit ($\mu\text{g L}^{-1}$)	RSD (%)	References
IL-DPME	HPLC	0.5–2000	0.15	4.7	[23]
Without extraction	Electrochemical sensor	9–549	2.7	6.8	[24]
Without extraction	Spectrophotometry	0-10	-	4.2	[25]
IEME	HPLC	1.00–80	1.0	6.1	[26]
CPE	Spectrophotometry	0.05–5.00	37.19	3.2	[27]
UA-IL-FODME	Spectrophotometry	10-700	3.2	2.2	This study

Ionic liquid dispersive phase microextraction (IL-DPME), high-performance liquid chromatography (HPLC), in-tube electro-membrane extraction (IEME), ultrasound-assisted ionic liquid-based floating organic droplets microextraction (UA-IL-FODME)

4. CONCLUSION

In this study, a simple, innovative and inexpensive ultrasound-assisted ionic liquid-based floating organic droplets microextraction (UA-IL-FODME) method was proposed for the extravasation of synthetic food dye tartrazine in soft drinks and foodstuff. The amount of tartrazine was determined by spectrophotometer. The extraction of tartrazine was provided in the mixture of ionic liquid ([C8MIM][BF₄]) and dispersive solvent (1-octanol) at pH 5.5. The ultrasonic bath temperature during extraction was 45 °C. The most important advantages of the method were the use of chemicals in μL levels to ensure extraction. The use of environmentally friendly, inexpensive chemical and experimental material, rapid extraction, wide linear range, low detection limit are other outstanding advantages of the method. Detailed selectivity and validation studies were performed. The method was successfully applied to the extraction and determination of the tartrazine in selected samples. The results of recovery and RSD% were acceptable.

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