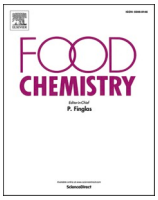
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Environmentally-friendly supramolecular solvent microextraction method for rapid identification of Sudan I–IV from food and beverages☆

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ABSTRACT

A new ultrasonically assisted supramolecular solvent-based microextraction (UA-SUPRAS-ME) method has been reported. This technique is one of the green methods for rapid microextraction and determination of Sudan I, II, III and IV dyes from food and beverage samples and the study investigated the effects of various parameters such as centrifugation time, 1-octanol volume, pH, supramolecular solvent type, THF volume, ultrasonication time on the optimization of the microextraction process. Addition and recovery of the method were carried out at two different concentrations (10 and 100 ng mL^{-1}) to food and beverage samples and the accuracy of the method was determined. Sudan I dye was detected in red pepper and hot sauce from food samples. Extraction recovery values were found between 90.6 % and 102.5 % which are promising compared to many other methods.

1. Introduction

Color is one of the important elements in the production and marketing of food and beverage products to increase the appeal of the products. For this reason, synthetic dyes are frequently used in food and beverage products. Although the application of many dyes is legally permitted in the production of these consumables, some dyes are added without permission. One of these synthetic dyes is Sudan dyes.

Sudan dyes (Sudan I, Sudan II, Sudan III, Sudan IV) are among the azo dyes (Fig. 1) containing a wide color scale and are phenyl-azoic derivatives that are frequently used in industries such as food, fabric, leather, cosmetics, plastics. They are used in many materials in order to keep the tone of the colors as well as, to make the materials more attractive and at the same time cut the production costs (López-Jiménez et al., 2010). Although these dyes are frequently used, various studies reported their effects on tumor formation in the bladder and liver of experimental animals (such as rabbit, mouse, rat) (Stiborová et al., 2002). In another study, it was reported that some of the intestinal bacterial species in humans can convert Sudan dyes into some aromatic amine species with carcinogenic properties. Considering the studies carried out, it reveals the risks of using these dyes (Xu et al., 2007). Despite the apparent adverse health effects of these dyes, they are still being used intensively, especially in food and beverage products. For this reason, it would be beneficial to develop a method for the separation and enrichment of Sudan dyes in food and beverage products.

Nowadays, capillary electrophoresis (Moreno-González et al., 2020), plasmon resonance light scattering (Wu et al., 2006), humic acid bonded silica solid phase extraction (Zheng, et al., 2007) electrochemical analytical methods (Du et al., 2007), liquid capillary chromatography (Benmassaoud et al., 2017), ultraviyole-visible (UV–Vis) spectrometry (Racheva et al., 2021), chemiluminescence coated electrokinetic capillary chromatography (Zhang et al., 2006) methods are used for the analysis of Sudan dyes in both solid and liquid samples. In addition to these methods, quadrupole flight tandem mass spectrometry, ultra-high performance liquid chromatography (U-HPLC) (Wozniak et al., 2021), ultraviolet visible detection HPLC (Ertas et al., 2007), ultra-fast liquid chromatography (Xu et al., 2015) methods are more frequently preferred. Although many methods have been proposed, HPLC is the most preferred method with its high sensitivity among these methods.

In chromatographic analysis, separation-enrichment methods should be applied to obtain more sensitive and accurate results before the analyte is injected into the HPLC system. Methods such as solid-phase extraction (SPE) and liquid-phase extraction (LPE), which are classical techniques, require large sample volumes (Hoseininezhad-Namin et al., 2022). These methods are also very time consuming and cause environmental problems as they require the use of high amounts of organic

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solvents. Due to the aforementioned reasons, fast, low-cost, environmentally friendly (Sivrikaya, 2020), low solvent volume-requiring microextraction methods and highly selective separation-enrichment methods are being developed in accordance with the new generation green principles for the determination of dye, preservatives and other components (Sivrikaya, 2019; Dalmaz & Sivrikaya Özak, 2022; Altunay, 2021; Dalmaz & Özak, 2022a; Rezaee et al., 2010; Dalmaz & Özak, 2022b).

To perform microextraction of Sudan I–IV dyes from food, beverage and cosmetic various methods have been developed (such as; cloud point microextraction (Shi & Chen, 2014), dispersive liquid–liquid microextraction (Unsal et al., 2014), surfactant-mediated microextraction using exchangeable hydrophilic solvent (Pochivalov et al., 2018), ultrasound-assisted hydrophobic DES (deep eutectic solvent)-based solid–liquid microextraction (Ozak & Yılmaz, 2020), nonionic surfactants-based hydrophobic deep eutectic solvent assisted liquid–liquid microextraction (Chen et al., 2021), natural deep eutectic solvent (Liu et al., 2019), membrane filtration (ALOthman et al. 2012), ultrasound-assisted magnetic-SPE (Duman et al., 2020). As an alternative to these methods, supramolecular solvent-based microextraction methods have currently become the recent way in most studies.

Supramolecular solvents (SUPRAS) are new generation chemicals emerging as an alternative to organic solvents. SUPRAS, which is immiscible with water, also has a nano structure. It arises through the spontaneous formation of reverse micelle aggregates of alkanols in a mixture of tetrahydrofuran and water (Ballesteros-Gómez & Rubio, 2012). It interacts with molecules in a wide range of polarity regions. These unique features ensure considerable reduction in extraction time and increment in extraction efficiency making SUPRAS's some more preferred extraction methods for inorganic and organic analytes from solid and liquid samples. Liquid phase microextraction has attracted attention as an environmentally friendly, low cost and fast method during sample preparation. When the literature is examined, supramolecular solvent microextraction studies have been reported in many samples, including soil (Caballo et al., 2014), endocrine disruptors (López-Jiménez et al., 2013), polycyclic aromatic carbons (Caballero-Casero et al., 2015) and foods (García-Fonseca et al., 2016).

In the present study, ultrasonic-assisted supramolecular solvent-based microextraction method, which is one of the new generation green methods, has been developed as an alternative to classical methods for the determination of Sudan dyes. While developing the method for the samples, centrifugation time, 1-octanol volume, pH, solvent type, THF volume, ultrasonic time were determined as optimization parameters. In this study, the existence of Sudan I, Sudan II, Sudan III and Sudan IV dyes in chilli sauce, red pepper, red wine, and powder beverage products were investigated under different experimental parameters (i.e., centrifugation time, pH, etc.). Moreover, it should be underlined that to the best of our knowledge, the supramolecular solvent microextraction method is the first to be used for simultaneous detection of Sudan I–IV dyes in different samples.

2. Materials and methods

2.1. Chemicals, reagent and calibration standards

All chemicals and reagents used during the experiments were disposed in analytical purity without purification. During the study, deionized water was used in every step and Sudan dyes (I, II, III, IV) used as standard material were obtained from Sigma Aldrich (St. Loius, MO, USA). HPLC grade methanol and acetonitrile, tetrahydrofuran and 1-octanol were purchased from Merck (Darmstadt, Germany). During the study, Millipore Milli Q (Millipore, Billerica, MA, USA) treatment system was used as an ultrapure water source. Stock solutions of Sudan I, Sudan II, Sudan III, Sudan IV dyes were prepared in methanol at a concentration of 1000 μg mL^{-1} and the prepared stock solutions were stored at 4 °C. All standard solutions to be used during the study were prepared by appropriate dilution using methanol as solvent. In the study, phosphate and acetate buffer solutions were prepared and their applications were carried out to examine the pH effect.

2.2. Sample preparation

Red wine, powdered beverage, chili sauce and red pepper samples were purchased from local markets in Düzce. Samples of powdered beverage, chili sauce and red pepper (20 mg each), red wine (1 mL) were dissolved in 50 mL methanol. The developed method was studied by taking the sample volume of 1 mL, which was determined in the study, from the dissolved food and beverage samples. The products that did not contain Sudan dyes were used for method's optimization. In addition, Sudan dyes standards at different concentrations were added to the study samples and the UA-SUPRAS-ME method was applied to different food and beverage samples.

2.3. Instruments

Electronic balance (Weightlab Instruments, Istanbul, Turkey) was

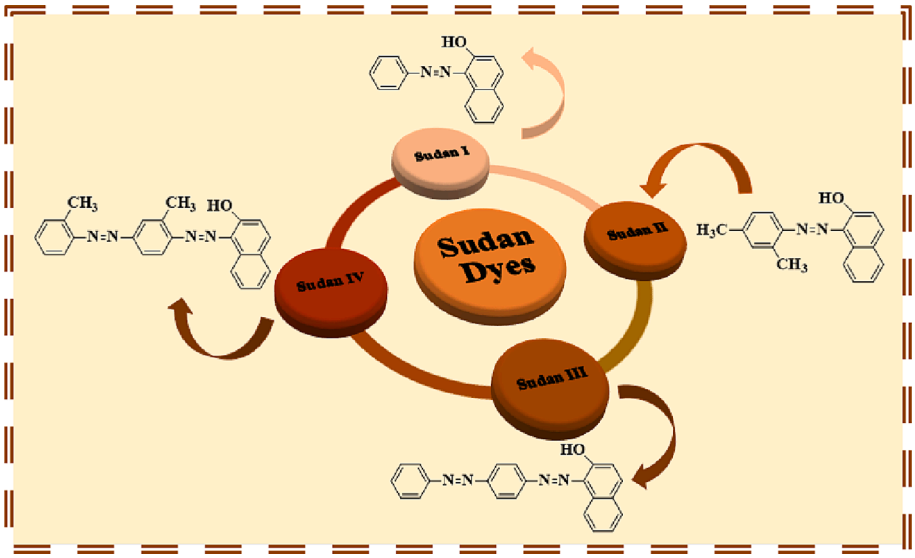


Fig. 1. Representation of molecular structures of Sudan I–IV dyes.

used during the optimization studies and weighing the materials used during the study. While performing the experimental studies, pH meter (AZ Instrument, China) was used for pH measurements and pH optimization of both real samples and model solutions. Elektromag (Istanbul, Turkey) brand M 2815P model centrifuge was used to perform the separation of the SUPRAS phase. Model solutions of food and beverage samples and microextraction of Sudan dyes from the samples were carried out using ultrasonic bath of Hydraultrasonic brand.

HPLC-UV (Shimadzu, Japan) device was used to perform chromatographic analysis of Sudan dyestuffs from food and beverage samples. Sudan dyes were determined at the wavelength of 480 nm with an isocratic pump and UV detector. During the experiments, separation was carried out by means of an ODS-C18 column (Welchrom) with an internal diameter of 4.6 mm, a length of 250 mm and a particle size of 5 μm. The mobile phase consisting of methanol (solvent A) and acetonitrile (solvent B) solvents was prepared. The mobile phase composition consisting of 80 % solvent A and 20 % solvent B was used in the study. In addition, the injection volume was adjusted to 20 μL, and the solvent elution was performed at a flow rate of 1 mL min^{-1}.

2.4. Optimization parameters

In this study, the optimization of 6 different parameters affecting the extraction recovery, including supramolecular solvent type, THF volume, 1-octanol volume, solution pH, centrifuge and ultrasonic time were investigated. As a consequence, both the presence and concentration of Sudan dyes in real samples (food and beverage samples) were determined according to the optimization parameters. During the study, the experiments were carried out in 3 repetitions and the optimization parameters were obtained as the average of these repetition outcomes.

2.5. UA-SUPRAS-ME test procedure

Fig. 2 shows the schematic representation of the developed UA-SUPRAS-ME test procedure (Soylak et al., 2020). After 1000 μL volume of sample solutions were taken into the conic-bottom falcon tube, 200 μL 1-octanol and 200 μL THF were added to the falcon tube to form the SUPRAS phase. 3 mL of pH 4.0 buffer (acetic acid/sodium acetate) was then added to this mixture and the sample volume was made up to 15 mL with deionized water. Supramolecular solution was formed by exposing the prepared solution to ultrasonic vibration for 4 min. Following this step, the cloudy solution was centrifuged at 4000 rpm for 4 min to accelerate the separation of the supramolecular solvent phase. After the supramolecular solvent phase was separated as supernatant, it was injected into the HPLC-UV system for the analysis of Sudan dyes.

3. Result and discussions

3.1. Effect of solution pH

The pH of the sample solution plays an important role in the extraction recoveries. In order to investigate the effect of pH on the microextraction recovery of Sudan dyes, the pH values of the prepared samples were adjusted to be varying between 2 and 10 by adding different buffer solutions. The effect of pH on extraction recovery was explained by the results in Fig. 3 (a). The obtained results show that the quantitative extraction efficiency for Sudan dyes was obtained at pH 4.0 and higher of the sample solution. pH of solution was adjusted pH 4.0 buffer with acetic acid/sodium acetate. For this reason, 4.0 was chosen as the optimal pH in this study conducted with the developed UA-SUPRAS-ME method.

3.2. Types of disperser and extraction solvents

As reverse micelles are produced by the combination of 1-octanol and THF, a supramolecular solvent is formed. Reversed micelles in the supramolecular solvent form by a dual mechanism for the dissolution of Sudan dyes. This mechanism is based on the Van der Waals hydrocarbon chains of 1-octanol and the hydrogen bond interactions in the micelle core. In this way, the extraction of Sudan dyes from the samples is carried out efficiently (López-Jiménez et al., 2010, Bogdanova et al., 2022).

In extraction studies using supramolecular solvent, the type and amount of extraction and disperser solvents are essential. In order to obtain the most suitable supramolecular solvent for the extraction of Sudan dyes, five different extraction solvent trials were carried out: 1-octanol, 1-decanol, decanoic acid, undecanoic acid and 1-butanol. The solvent used as the extraction solvent is desired to have advantages such as low toxicity, melting point at room temperature, low volatility, and good solubility. 1-octanol is a good extraction solvent with these properties. THF used in the production of supramolecular solvent has two functions. One is that it is a disperser solvent, and the other causing the self-assembly of 1-octanol. When Fig. 3 (b) was examined, it could be seen that the best recovery values of Sudan dyes were obtained when THF and 1-octanol were used as disperser and extraction solvents, respectively. For this reason, a supramolecular solvent was created using THF and 1-octanol and used in the study.

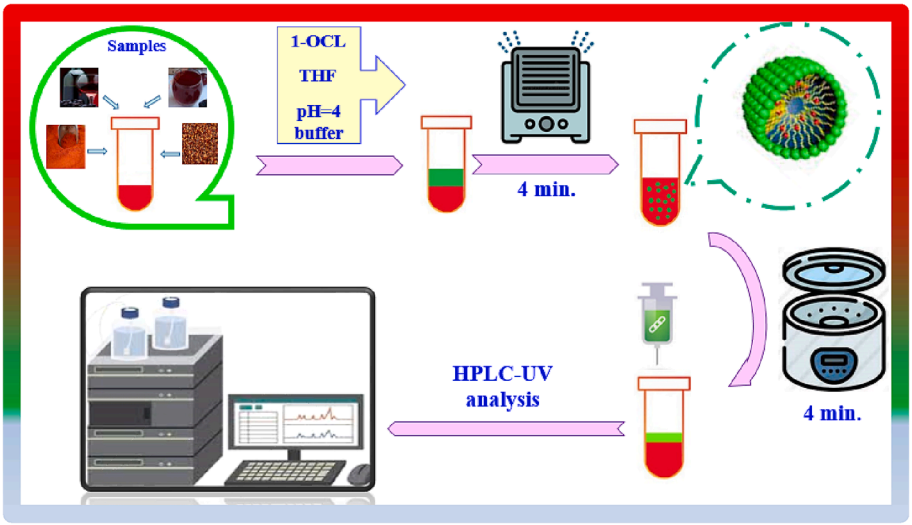


Fig. 2. The shematic procedure of UA-SUPRAS-ME.

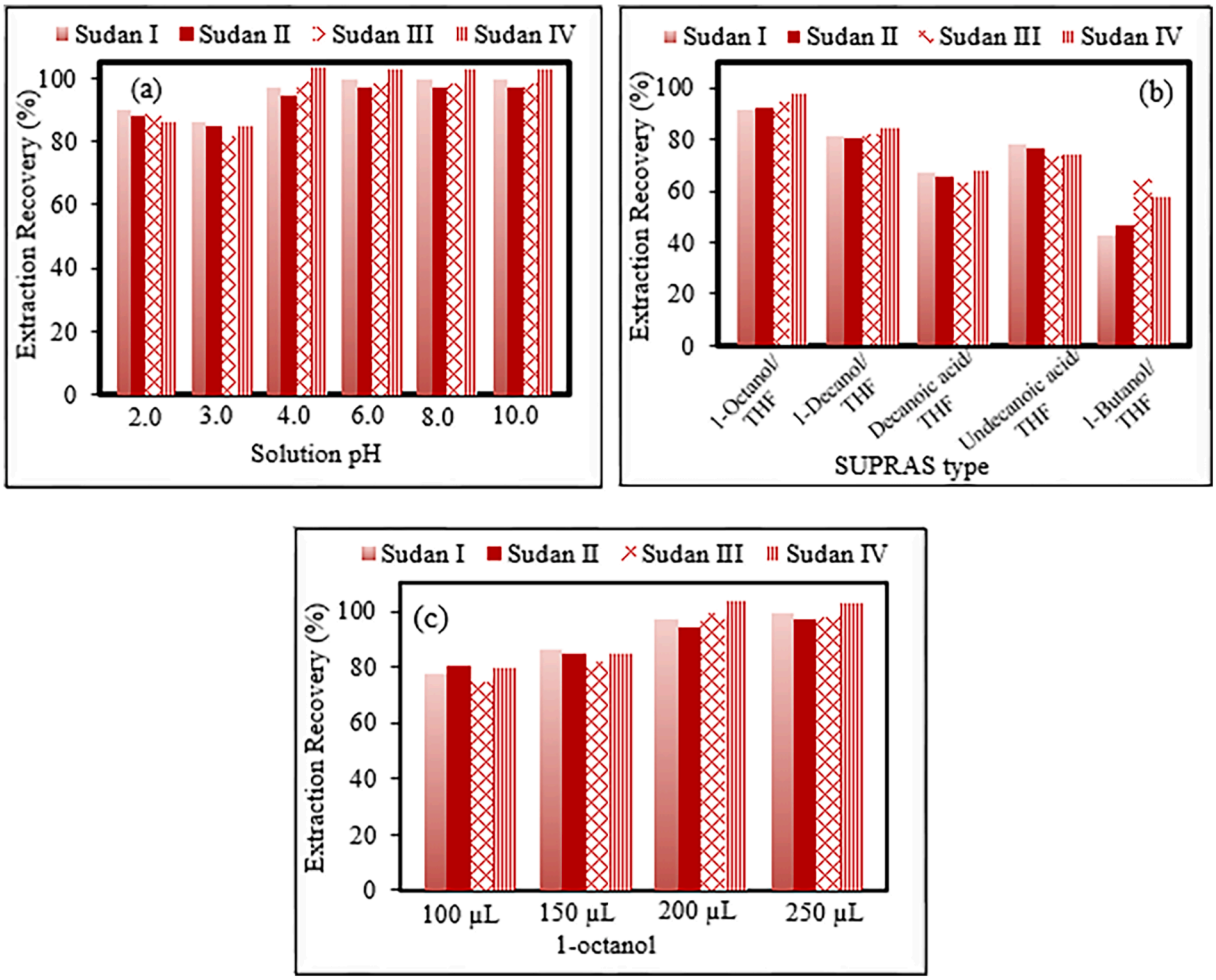


Fig. 3. Effect of solution pH (a), supramolecular solvent type (b), extraction solvent (1-octanol) (c) on the extraction of Sudan dyes (N = 3).

3.3. Volume of extraction solvent

In order to examine the effect of the change in the volume of the extraction solvent in the developed UA-SUPRAS-ME method, the changes were examined by using varying volumes of 1-octanol (100–250 µL). Extraction recovery values obtained for Sudan dyes were given in Fig. 3 (c). The results show that the use of up to 200 µL of 1-octanol, the extraction recovery increased and remained constant thereafter. Therefore, 200 µL of 1-octanol used as extraction solvent in subsequent experiments.

3.4. Disperser solvent volume

After selecting the extraction solvent and its volume, another important parameter is adjusting the volume of the disperser solvent. Samples were prepared under the same operating conditions using THF (i.e., the disperser solvent) varying in volumes ranging from 100 to 500 µL containing 200 µL 1-octanol, and the developed UA-SUPRAS-ME method was applied. The results show that the best extraction recovery was achieved when 200 µL of THF was used (Fig. 4 (a)). When 100 µL of THF was used, the recovery values were low because the coacervation process did not occur due to the low volume. Therefore, 200 µL of THF was selected and applied in the study as the disperser solvent.

3.5. Effect of ultrasonication time

It is aimed to produce intense cavitation on the solvent by using ultrasonic waves. Therefore, increasing the interaction between Sudan dyes and the extraction solution would result in enhancing the efficiency and the performance of the method. An ultrasound energy of 100 W and 40 kHz was applied to induce the formation of a thin cloudy solution. In this study, the effect of ultrasonic waves on extraction recovery was investigated in the range of 2 to 10 min (Fig. 4 (b)). The quantitative recovery values were obtained when the ultrasonication time reached 4.0 min. Therefore, in this study, 4.0 min was found to be sufficient for the ultrasonication process.

3.6. Effect of centrifugation time

In order to examine the effect of centrifugation time on the extraction recovery of Sudan dyes, it was investigated in the range of 2–10 min. In the developed method, a centrifuge time of 4 min at 4000 rpm was chosen in order to obtain a complete separation of Sudan dyes, and it was observed that there was no change in extraction yields when the centrifuge was increased further (Fig. 4 (c)). For this reason, 4 min was used as the centrifugation time in the study.

3.7. Analytical performance

Linear range, linear equations, correlation coefficients (R^2), limit of detection (LOD), limit of quantification (LOQ), and relative standard deviation (RSD) for the developed UA-SUPRAS-ME method are investigated. Calibration curves were generated in the concentration range of 1–100 ng mL^{-1} under the specified optimization conditions. The correlation coefficients value greater than 0.9952 indicated excellent linearity for the concentration range studied. LODs and LOQ values were

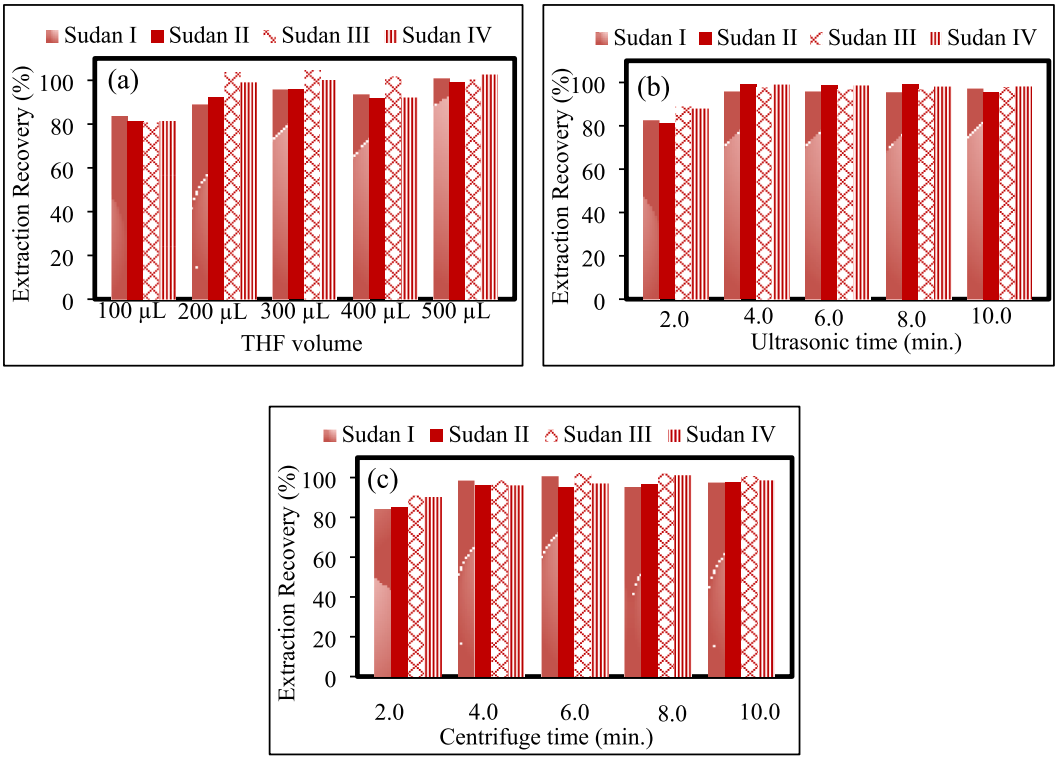


Fig. 4. Effect of the volume of disperser solvent (THF) (a), ultrasonic time (b), centrifugation time (c) on the extraction of Sudan dyes (N = 3).

in the range of 0.48–0.63 ng mL^{-1} and 1.60–2.09 ng mL^{-1}, respectively, indicating that the developed method has high sensitivity. RSD values were found to be less than 2.47 for 10 ng mL^{-1} Sudan I–IV dyes indicated the reproducibility of the analysis.

3.8. Applications

The developed UA-SUPRAS-ME method was applied for the presence and determination of Sudan dyes in red wine, powder beverage, chili sauce, and red pepper. The samples were purchased from various local markets in Düzce, Turkey. When the results in Table 1 were examined, the presence of Sudan I dye was detected in 2 of 4 different samples (hot sauce and red pepper). With the developed method, the food and beverage samples to be analyzed were first examined without any addition, then by adding Sudan I–IV dye standards at 10–100 ng mL^{-1} concentrations to evaluate the accuracy. The recovery values obtained in the results in Table 1 show that good recoveries were obtained in the range of 90.9–102.5 %. The results demonstrate the accuracy of the developed method for the extraction and determination of Sudan I–IV dyes in food and beverage samples. In addition, the analysis of the chili sauce sample, which contains Sudan dyes, with the developed method, and the chromatograms obtained as a result of the analyzes at 10 and 100 ng mL^{-1} concentrations were given in Fig. S1 in the supplementary material.

3.9. Comparison of UA-SUPRAS-ME method performance

Table 2 presents a comparison of the method developed in this study with other methods in the previously developed literature for the determination of Sudan dyes in food and beverage samples. When the results are examined, it is seen that the UA-SUPRAS-ME method developed in this study is comparable to the other literature studies given in Table 2. In addition, the accuracy of the method developed in this study found to be sufficient from the obtained extraction recovery values. The method in this study has proved to be advantageous as dispersion and extraction solvents are simple to synthesize. Moreover, it has got

Table 1
The recoveries obtained from the determination of Sudan I–IV dye in different samples by developed UA-SUPRAS-ME method (N = 3).

		Sudan I		Sudan II		Sudan III		Sudan IV	
Sample	Spiked (ng mL^{-1})	Found	%R	Found	%R	Found	%R	Found	%R
Red wine	0	N.D.	–	N.D.	–	N.D.	–	N.D.	–
	10	9.1	90.8	10.2	101.5	9.6	96.1	9.3	92.5
	100	91.8	91.8	90.9	90.9	97.2	97.2	94.0	94.0
Powder beverage	0	N.D.	–	N.D.	–	N.D.	–	N.D.	–
	10	10.1	101.1	9.6	96.2	9.8	97.5	9.4	93.9
	100	102.2	102.2	93.8	93.8	95.6	95.6	90.9	90.9
Chili sauce	0	13.1	–	N.D.	–	N.D.	–	N.D.	–
	10	22.7	98.6	9.3	92.9	9.8	98.3	9.4	93.5
	100	107.5	94.5	91.6	91.6	97.7	97.7	90.7	90.7
Red pepper	0	28.5	–	N.D.	–	N.D.	–	N.D.	–
	10	37.8	98.3	9.1	90.6	9.7	97.0	9.3	93.2
	100	131.7	102.5	94.2	94.2	93.5	93.5	94.3	94.3

N.D: not detected.

Table 2
Comparison of UA-SUPRAS-ME method with different extraction methods.

Procedure	Instrument	Analyte	Matrix	LOD (ng mL^{-1})	Recovery (%)	EF	Ref.
SUPRAS-LPME[a]	UV–Vis	Sudan I–IV	Chili powder, water samples	1.74	101–108	20	Soylak et al. (2021)
UADLLME-SFO[b]	HPLC-PDA	Sudan I	Tomato sauce, chili products	1.5	79–92	–	He et al. (2015)
SPE[c]	HPLC-DAD	Sudan I–IV	Chili products	4.1–5.8	93.2–103	–	Qi et al. (2011)
LPME[d]	UV–Vis	Sudan dyes	Chili powder, chili sauce, ketchup	0.5–1.0	86.3–90.9	92–97	Ge et al. (2021)
LPME[e]	UV–V is	Sudan Orange G	Artificial sweat, tap water, sea water	3.4	91–109	40	Soylak et al. (2020)
OS-AALLME[f]	HPLC-UV	Sudan I–IV, Sudan Orange G	Human plasma, urine, Lipstick	3.9–84.8	86.8–102.3	33–39	Barfi et al. (2015)
UA-SUPRAS-ME	HPLC-UV	Sudan I–IV	Red wine, powder beverage, chili sauce, red pepper	0.48–0.63	90.6–102.5	75	Present work

[a] Ultrasound assisted supramolecular liquid phase microextraction.
[b] Ultrasound-assisted dispersive liquid–liquid microextraction with solidification of floating organic drop.
[c] Solid phase extraction.
[d,e] Liquid phase microextraction.
[f] Organic solvent-free air-assisted liquid–liquid microextraction.

superior features as low detection limit of extraction recovery values and computational efficiency (i.e., economical, fast, simultaneous detection of Sudan I–IV dyes) but most importantly environmentally friendly.

4. Conclusions

The green, fast and novel UA-SUPRAS-ME procedure is presented as a microextraction method developed for extraction and quantification of Sudan dyes found in food and beverage samples. In this study, optimization of all parameters was performed for the recovery of the analyte from the samples. At the same time, this developed method can be applied to samples in as little as 10 min. Moreover, this developed method has advantages such as using green chemicals, short extraction time, being a low cost and practical method, requiring the use of very low solvent volume, being environmentally friendly, requiring minimal use of organic solvents, being selective and sensitive. When the results are examined, it shows that this developed method can be successfully applied to many samples similar to the samples in this study. This can be understood from the high extraction recovery values. In addition, the applicability of the method was evaluated by determining the value of Sudan dyes in different food and beverage samples.

CRediT authorship contribution statement

Aslihan Dalmaz: Data curation, Investigation, Funding acquisition, Writing – original draft. **Sezen Sivrikaya Özak:** Conceptualization, Methodology, Writing – original draft, Supervision, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.foodchem.2023.135713.

References

ALOthman, Z. A., Unsal, Y. E., Habila, M., Shabaka, A., Tuzen, M., & Soylak, M. (2012). Membrane filtration of Sudan orange G on a cellulose acetate membrane filter for separation–preconcentration and spectrophotometric determination in water, chili powder, chili sauce and tomato sauce samples. *Food and Chemical Toxicology, 50*(8), 2709–2713. https://doi.org/10.1016/j.fct.2012.05.021

Altunay, N. (2021). Optimization of ultrasound-assisted dispersive liquid–liquid microextraction of niacinamide in pharmaceutical and cosmetic samples using experimental design. *Microchemical Journal, 170*, Article 106659. https://doi.org/10.1016/j.microc.2021.106659

Ballesteros-Gómez, A., & Rubio, S. (2012). Environment-responsive alkanol-based supramolecular solvents: Characterization and potential as restricted access property and mixed-mode extractants. *Analytical chemistry, 84*(1), 342–349. https://doi.org/10.1021/ac2026207

Barfi, B., Asghari, A., Rajabi, M., & Sabzalian, S. (2015). Organic solvent-free air-assisted liquid–liquid microextraction for optimized extraction of illegal azo-based dyes and their main metabolite from spices, cosmetics and human bio-fluid samples in one step. *Journal of chromatography B, 998*, 15–25. https://doi.org/10.1016/j.jchromb.2015.06.016

Benmassaoud, Y., Villaseñor, M. J., Salghi, R., Jodeh, S., Algarra, M., Zougagh, M., & Ríos, Á. (2017). Magnetic/non-magnetic argan press cake nanocellulose for the selective extraction of sudan dyes in food samples prior to the determination by capillary liquid chromatograpy. *Talanta, 166*, 63–69. https://doi.org/10.1016/j.talanta.2017.01.041

Bogdanova, P., Vakh, C., & Bulatov, A. (2022). A surfactant-mediated microextraction of synthetic dyes from solid-phase food samples into the primary amine-based supramolecular solvent. *Food Chemistry, 380*, Article 131812. https://doi.org/10.1016/j.foodchem.2021.131812

Caballero-Casero, N., Çabuk, H., Martínez-Sagarra, G., Devesa, J. A., & Rubio, S. (2015). Nanostructured alkyl carboxylic acid-based restricted access solvents: Application to the combined microextraction and cleanup of polycyclic aromatic hydrocarbons in mosses. *Analytica chimica acta, 890*, 124–133. https://doi.org/10.1016/j.aca.2015.06.060

Caballo, C., Sicilia, M. D., & Rubio, S. (2014). Fast, simple and efficient supramolecular solvent-based microextraction of mecoprop and dichlorprop in soils prior to their enantioselective determination by liquid chromatography–tandem mass spectrometry. *Talanta, 119*, 46–52. https://doi.org/10.1016/j.talanta.2013.10.043

Chen, J., Li, X., Huang, A., Deng, W., & Xiao, Y. (2021). Nonionic surfactants based hydrophobic deep eutectic solvents for liquid–liquid microextraction of Sudan dyes in tomato chili sauces. *Food Chemistry, 364*, Article 130373. https://doi.org/10.1016/j.foodchem.2021.130373

Dalmaz, A., & Özak, S. S. (2022a). DES-based vortex-assisted liquid-liquid microextraction procedure developed for the determination of paraben preservatives in mouthwashes. *Microchemical Journal, 179*, Article 107445. https://doi.org/10.1016/j.microc.2022.107445

Dalmaz, A., & Özak, S. S. (2022b). Development of clinoptilolite zeolite-coated magnetic nanocomposite-based solid phase microextraction method for the determination of Rhodamine B in cosmetic products. *Journal of Chromatography A.* , Article 463433. https://doi.org/10.1016/j.chroma.2022.463433

Dalmaz, A., & Sivrikaya Özak, S. (2022). Green deep eutectic solvent assisted liquid–liquid microextraction procedure for Sunset Yellow dye in effervescent vitamin C tablets. *Journal of the Iranian Chemical Society, 19*(6), 2359–2366. https://doi.org/10.1007/s13738-021-02454-y

Du, M., Han, X., Zhou, Z., & Wu, S. (2007). Determination of Sudan I in hot chili powder by using an activated glassy carbon electrode. *Food Chemistry, 105*, 883–888. https://doi.org/10.1016/j.foodchem.2006.12.039

Duman, S., Erbas, Z., & Soylak, M. (2020). Ultrasound-assisted magnetic solid phase microextraction of patent blue V on magnetic multiwalled carbon nanotubes prior to its spectrophotometric determination. *Microchemical Journal, 159*, Article 105468. https://doi.org/10.1016/j.microc.2020.105468

Ertas, E., Ozer, H., & Alasalvar, C. (2007). A rapid HPLC method for determination of Sudan dyes and Para Red in red chili pepper. *Food Chemistry, 105*, 756–760. https://doi.org/10.1016/j.foodchem.2007.01.010

García-Fonseca, S., Ballesteros-Gómez, A., & Rubio, S. (2016). Restricted access supramolecular solvents for sample treatment in enzyme-linked immuno-sorbent assay of mycotoxins in food. *Analytica Chimica Acta, 935*, 129–135. https://doi.org/10.1016/j.aca.2016.06.042

Ge, D., Shan, Z., Pang, T., Lu, X., & Wang, B. (2021). Preparation of new hydrophobic deep eutectic solvents and their application in dispersive liquid–liquid microextraction of Sudan dyes from food samples. *Analytical and Bioanalytical Chemistry, 413*(15), 3873–3880. https://doi.org/10.1007/s00216-021-03337-0

He, X., Chen, Y., Li, H., Zou, T., Huang, M., Li, H., & Xia, E. (2015). Analysis of Sudan I in food by QuEChERS combined with ultrasound-assisted dispersive liquid-liquid microextraction with solidification of floating organic drop (UADLLME-SFO) prior to HPLC-PAD. *Food Science and Technology Research, 21*(5), 659–664. https://doi.org/10.3136/fstr.21.659

Hoseininezhad-Namin, M. S., Rahimpour, E., Ozkan, S. A., & Jouyban, A. (2022). An overview on nanostructure-modified supported liquid membranes for the electromembrane extraction method. *Analytical Methods, Advancing Methods and Applications, 14*(3), 212–221. https://doi.org/10.1039/D1AY01833G

Liu, W., Zong, B., Wang, X., Cai, J., & Yu, J. (2019). A highly efficient vortex-assisted liquid–liquid microextraction based on natural deep eutectic solvent for the determination of Sudan I in food samples. *RSC Advances, 9*(30), 17432–17439. https://doi.org/10.1039/c9ra01405e

López-Jiménez, F. J., Rosales-Marcano, M., & Rubio, S. (2013). Restricted access property supramolecular solvents for combined microextraction of endocrine disruptors in sediment and sample cleanup prior to their quantification by liquid chromatography–tandem mass spectrometry. *Journal of Chromatography A, 1303*, 1–8. https://doi.org/10.1016/j.chroma.2013.06.043

López-Jiménez, F. J., Rubio, S., & Pérez-Bendito, D. (2010). Supramolecular solvent-based microextraction of Sudan dyes in chilli-containing foodstuffs prior to their liquid chromatography-photodiode array determination. *Food Chemistry, 121*(3), 763–769. https://doi.org/10.1016/j.foodchem.2009.12.081

Moreno-González, D., Jáč, P., Švec, F., & Nováková, L. (2020). Determination of Sudan dyes in chili products by micellar electrokinetic chromatography-MS/MS using a volatile surfactant. *Food Chemistry, 310*, Article 125963. https://doi.org/10.1016/j.foodchem.2019.125963

Ozak, S. S., & Yılmaz, Y. (2020). Ultrasound-assisted hydrophobic deep eutectic solvent based solid-liquid microextraction of Sudan dyes in spice samples. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 236*, 118353. https://doi.org/10.1016/j.saa.2020.118353

Pochivalov, A., Davletbaeva, P., Cherkashina, K., Lezov, A., Vakh, C., & Bulatov, A. (2018). Surfactant-mediated microextraction approach using switchable hydrophilicity solvent: HPLC-UV determination of Sudan dyes in solid food samples. *Journal of Molecular Liquids, 271*, 807–814. https://doi.org/10.1016/j.molliq.2018.09.072

Qi, P., Zeng, T., Wen, Z., Liang, X., & Zhang, X. (2011). Interference-free simultaneous determination of Sudan dyes in chili foods using solid phase extraction coupled with HPLC–DAD. *Food Chemistry, 125*(4), 1462–1467. https://doi.org/10.1016/j.foodchem.2010.10.059

Racheva, P. V., Milcheva, N. P., Genc, F., & Gavazov, K. B. (2021). A centrifuge-less cloud point extraction-spectrophotometric determination of copper (II) using 6-hexyl-4-(2-thiazolylazo) resorcinol. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 262*, Article 120106. https://doi.org/10.1016/j.saa.2021.120106

Rezaee, M., Yamini, Y., & Faraji, M. (2010). Evolution of dispersive liquid–liquid microextraction method. *Journal of Chromatography A, 1217*(16), 2342–2357. https://doi.org/10.1016/j.chroma.2009.11.088

Shi, J., & Chen, L. (2014). Analysis of Sudan dyes in lipstick samples by cloud-point extraction and high-performance liquid chromatography. *Analytical Methods, 6*(20), 8129–8135. https://doi.org/10.1039/C4AY00814F

Sivrikaya, S. (2019). A novel vortex-assisted liquid phase microextraction method for parabens in cosmetic oil products using deep eutectic solvent. *International Journal of Environmental Analytical Chemistry, 99*(15), 1575–1585. https://doi.org/10.1080/03067319.2019.1625345

Sivrikaya, S. (2020). A vortex-assisted microextraction based on deep eutectic solvents for determination of four parabens from cosmetic baby oils and optimization by Box-Behnken design. *Düzce Üniversitesi Bilim ve Teknoloji Dergisi, 8*(3), 1936–1947. https://doi.org/10.29130/dubited.721252

Soylak, M., Celik, M., & Uzcan, F. (2020). Supramolecular solvent-based microextraction of Sudan Orange G at trace levels for its separation, preconcentration and spectrophotometric determination. *International Journal of Environmental Analytical Chemistry, 100*(8), 935–944. https://doi.org/10.1080/03067319.2019.1645842

Soylak, M., Özalp, Ö., & Uzcan, F. (2021). Ultrasound assisted supramolecular liquid phase microextraction procedure for Sudan I at trace level in environmental samples. *Turkish Journal of Chemistry, 45*(5), 1327–1335. https://doi.org/10.3906/kim-2104-5

Stiborová, M., Martínek, V., Rýdlová, H., Hodek, P., & Frei, E. (2002). Sudan I is a potential carcinogen for humans: Evidence for its metabolic activation and detoxication by human recombinant cytochrome P450 1A1 and liver microsomes. *Cancer Research, 62*(20), 5678–5684.

Unsal, Y. E., Tuzen, M., & Soylak, M. (2014). Spectrophotometric determination of Sudan Blue II in environmental samples after dispersive liquid-liquid microextraction. *Química Nova, 37*, 1128–1131. https://doi.org/10.5935/0100-4042.20140192

Wozniak, M. M., Witkowski, B., Ganeczko, M., Gierczak, T., & Biesaga, M. (2021). Textile dyeing in Medieval Sudan evidenced by HPLC-MS analyses: Material traces of a disappeared activity. *Journal of Archaeological Science: Reports, 38*, Article 103098. https://doi.org/10.1016/j.jasrep.2021.103098

Wu, L. P., Li, Y. F., Huang, C. Z., & Zhang, Q. (2006). Visual detection of Sudan dyes based on the plasmon resonance light scattering signals of silver nanoparticles. *Analytical Chemistry, 78*(15), 5570–5577. https://doi.org/10.1021/ac0603577

Xu, B., Wang, Y., Jin, R., Li, X., Song, D., Zhang, H., & Sun, Y. (2015). Magnetic solid-phase extraction based on Fe_3O_4@polyaniline particles followed by ultrafast liquid chromatography for determination of Sudan dyes in environmental water samples. *Analytical Methods, 7*(4), 1606–1614. https://doi.org/10.1039/C4AY02645D

Xu, H., Heinze, T. M., Chen, S., Cerniglia, C. E., & Chen, H. (2007). Anaerobic metabolism of 1-amino-2-naphthol-based azo dyes (Sudan dyes) by human intestinal microflora. *Applied and Environmental Microbiology, 73*(23), 7759–7762. https://doi.org/10.1128/AEM.01410-07

Zhang, Y., Zhang, Z., & Sun, Y. (2006). Development and optimization of an a analytical method for the determination of Sudan dyes in hot chili pepper by high performance liquid chromatography with on-line electrogenerated BrO-luminol chemiluminiscence detection. *Journal of Chromatography A, 1129*(1), 34–40. https://doi.org/10.1016/j.chroma.2006.06.028

Zheng, M., Wu, J., Luo, D., Yu, Q., & Feng, Y. (2007). Determination of Sudan red dyes in hot chili products by humic acid-bonded silica solid-phase extraction coupled with high performance liquid chromatography. *Se Pu (Se pu = Chinese Journal of Chromatography), 25*(5), 619–622.