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A HYDROPHILLIC DEEP EUTECTIC SOLVENT ASSISTED MAGNETIC COLLOIDAL GEL BASED DISPERSIVE SOLID PHASE MICROEXTRACTION METHOD FOR PRECONCENTRATION OF BROWN HT (E155)

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ABSTRACT

A hydrophillic deep eutectic solvent assisted magnetic colloidal gel based dispersive solid phase microextraction method (MCG-dSPME) was developed for the pre-concentration of Brown HT (E155) before its spectrophotometric analysis. Magnetic colloidal gel was obtained from Fe_3O_4@XAD-7 nanoparticles and phenol/choline chloride (2:1) (hyrophillic deep eutectic solvent (DES). For the optimization of the developed method, several parameters such as pH, amount of Fe_3O_4@XAD-7 nanoparticles in the colloidal gel, volume of colloidal gel, type of desorption solvent, vortex time (for adsorption and desorption), sample volume were investigated. After determining the optimum conditions, the linear range, limit of detection (LOD), enhencament factor (EF), preconcentration factor (PF), relative standard deviation (RSD %) of the method were calculated. Then, addition/recovery test and intraday-interday test were applied for the accuracy and the precision, respectively. The matrix effect study was examined for the selectivity of the method. The linear range, LOD, RSD %, EF, and PF values of the method were found to be 0.05-0.75 mgL^{-1}, 0.016. mgL^{-1}, 3.8%, 51 and 25, respectively. The study was found to be no interference method with high accuracy and precision. In this study, according to our literature research, since there are very few studies on the determination of Brown HT, it was aimed to develop an up-to-date, economical, non-invasive, environmentally friendly and simple method for this dye.

Keywords: Magnetic colloidal gel, Dispersive solid phase microextraction method, Preconcentration, Spectrophotometric determination, Brown HT.

1 INTRODUCTION

Food coloring agents can be used to restore the original appearance of food in cases where the color of the food is affected by processing, storage, packaging and distribution, and

its visual acceptability is damaged, to make the food more visually attractive, and to give color to colorless food [1].

Brown HT (E 155, IC: 20285), whose chemical name is disodium 4,4'-(2,4-dihydroxy-5-hydroxymethyl-1,3-phenylene bis-azo) di- (naphthalene-1-sulfonate), (CAS No: 4553 -89-3) is a bis azo group food colorant. The molecular weight of this dye, which has the closed formula $C_{27}H_{18}N_4Na_2O_9S_2$, is 652.56 g/mol. This food colorant dissolves well in water and methanol[2]. The chemical structure of the dye is shown in Figure 1.

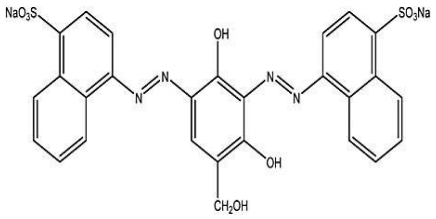


Figure 1. Chemical structure of Brown HT.

The maximum daily acceptable intake of Brown HT is 1.5 mg / kg-bw. Studies on mice with the dye have shown that it or its metabolites are absorbed in limited amounts and approximately 90% of this is excreted in the feces. It has also been observed that it accumulates in the lymph nodes and kidneys of mice [3].

According to the Turkish Food Codex, the maximum amount of Brown HT in foodstuffs/beverages is 50 $mgkg^{-1}$ or mgL^{-1} [1]. According to European Parliament and Council Directive 94/36/EC, the maximum usage levels in foodstuffs and beverages are 500 $mgkg^{-1}$ and 200 mgL^{-1}, respectively [3].

Brown HT is widely used as an additive in the food industry in soft drinks, flour, chocolate sauces, puddings, creams, candies and cookies[2-3]. Brown HT has been reported to be toxic to human at high concentrations. Because it has high water solubility, it can easily spread into the environment with industrial waste and harm animals. Like other azo dyes, Brown HT is also known as ecotoxic due to its harmful effects on the environment and public health. Therefore, the analysis of this dye is very important. Sensitive, accurate and reliable methods are needed for the analysis of this dye[4-8]. However, in our literature research, analysis methods for the determination of this dye are quite few]. Cloud point extraction-scanometry (CPE-scanometry) [9], UV-Vis spectrophotometer [10] and high-performance liquid chromatography/diode array detection (HPLC/DAD) [2], the cyclic voltammetry (CV) [11] methods are among the studies in the literature for the quantitative analysis of Brown HT.

Magnetic solid phase microextraction methods, unlike classical solid phase extraction methods, apply more miniature extraction processes. Smaller amounts of magnetic adsorbents and low volumes of extraction solvents are used. The advantage of magnetic adsorbents is that they can be easily removed from the solution with an external magnet. In magnetic dispersive solid phase microextraction methods, magnetic solid adsorbent is dispersed in the sample matrix to increase extraction efficiency [12-13]. In magnetic colloidal gel-based microextraction methods, the magnetic adsorbent is dispersed in a carrier liquid phase. This carrier liquid phase can be deep eutectic solvents, ionic liquids. It is thought that the sorbent obtained by mixing this material is better extracted since its association with the analyte increases [14].

Since the methods developed for the analysis of this dye are few in the literature, the main purpose of this study is to develop a sensitive, accurate and reliable method. In this study, magnetic amberlite XAD-7 nanoparticle was synthesized and characterized by TEM and FT-IR. A hydrophilic deep eutectic solvent (phenol/choline chloride, 2:1) based colloidal gel was created with magnetic amberlite XAD-7 nanoparticles. With the created colloidal gel, solid phase microextraction method was developed for the pre-concentration and separation of Brown HT. In the developed method, various parameters such as pH, composition of magnetic gel, type of desorption solvent, vortex time (for adsorption and desorption), sample volume were investigated. Then, the method was validated. Finally, the developed method was successfully applied to real samples.

2 MATERIALS AND METHOD

2.1 Apparatus

The spectra were recorded by a Carry 100 Bio UV-visible model double beam spectrophotometer, attached with 10.0 mm quartz cells was used for the absorbance measurements. A vortex (Velp brand) was used to facilitate the adsorption and desorption of Brown HT. A neodymium magnet with a strong magnetic field was used to remove nanoparticles from the solution. Infrared spectra of Fe_3O_4-XAD-7 and Fe_3O_4-XAD-7/DES were taken from an Agilent brand Cary 63 FT-IR model devices. The homogenous dispersion of the Fe_3O_4@XAD-7 nanoparticle in colloidal gel was investigated by Hitachi HT-7700 transmission electron microscope.

2.2 Reagents and Solutions

Choline chloride was taken from Glentham Life Sciences Ltd. (Corsham, United Kingdom). Phenol, Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), Iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Amberlite XAD-7, ammonia, acetonitrile, acetone, ethanol, methanol, and Brown HT were obtained from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions of 100 µg/mL of Brown HT prepared by dissolving distilled water in a 100 mL calibrated flask. Norateks (Istanbul, Turkey) brand buffer solutions were used for pH adjustments.

2.3 Preparation of DES, Fe_3O_4@ XAD-7 and Magnetic Colloidal Gel

For DES, choline chloride and phenol are mixed in 1:2 ratio in a capped conical flask. The mixture is stirred until it becomes clear. The transparent solution is left at room temperature [15].

Amberlite XAD-7 was added to a solution containing 1.0 M (mol.L^{-1}) Fe^{3+} and 2.0 M Fe^{2+} in 2.0 M HCl medium(1:2). After this mixture was stirred for 5 minutes, 1.0 M ammonia solution was slowly added until the solution turns to black. After the magnetic nanoparticles were formed, they were collected at the bottom of the conical flask with a neodymium magnet and the aqueous phase was removed and then the nanoparticles were washed with pure water and ethyl alcohol. The washed nanoparticles were then dried at 80 °C [15].

1.0 mL of DES and 60.0 mg of Fe_3O_4-XAD-7 magnetic nanoparticles were vortexed thoroughly in a tube until a homogenous black gel was obtained and then sonicated [15].

2.4 Real Sample Procedure

A real sample (chocolate souce) was taken from market in Diyarbakir, Türkiye. The appropriate amount of chocolate souce sample was weighed in the erlenmeyer. It was dissolved in 30 mL of water and transferred to volumetric flask. Then, the solution was diluted to 50 mL with pure water. The developed method was applied to 0.1 mL of this solution.

2.5 Analytical Procedure

20 mL of 0.5 mgL^{-1} Brown HT model solution was prepared at pH 4. Then, 0.4 mL of magnetic colloidal gel was added to the model solution. The solution was then vortexed for 10 minutes. The magnetic nanoparticles dispersed by vortexing were collected with a magnet and the water phase was decanted. Then, 0.8 mL of ammoniacal acetonitrile was added to the

nanoparticles loaded with the analyte. After vortexing this solution for 8 minutes, nanoparticles were collected on one side of the tube with the help of a magnet and the aqueous phase was removed. Then, the absorbance of the model solution was measured.

2.6 Carachterization of Fe_3O_4@XAD-7 and Fe_3O_4@XAD-7/DES

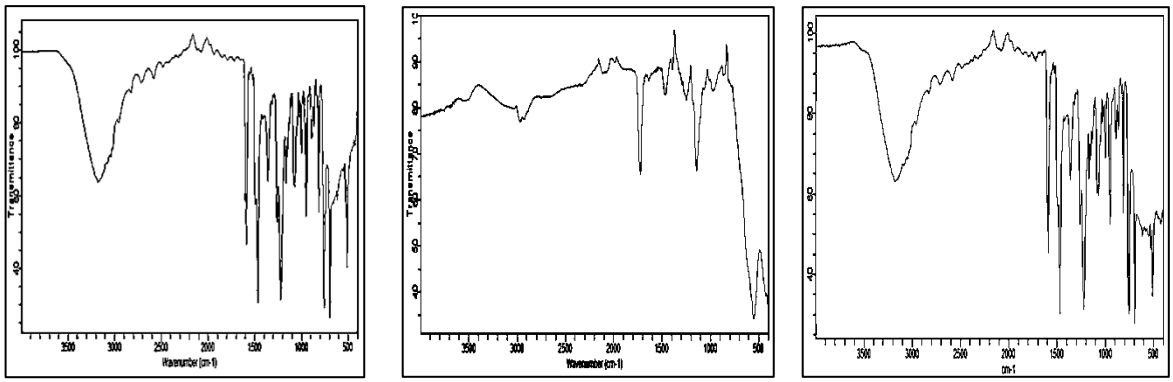
The structures of DES, Fe_3O_4@XAD-7 and Fe_3O_4@XAD-7/DES were characterized by Fourier transform infrared spectroscopy (FT-IR). As shown in Figure 2 (a), in the IR spectrum obtained for DES, the OH group of choline chloride and phenol in DES gives a broad band at 3000-3400 cm^{-1}, which meets the expectation. As shown in Figure 2 (b), the peak between 2850-3000 cm^{-1} for Fe_3O_4@XAD-7 can be related to the stretching vibration of the aliphatic C-H group in the structure of XAD-7. The broad peak at 500-600 cm^{-1} can be related to the Fe-O bond in the spectrum of the composite. As shown in Figure 2 (c), the broad peak between 3000-3400 cm^{-1} in the spectrum of Fe_3O_4@XAD–7/DES can be related to the O-H stretching vibration in the structure of both phenol and choline chloride in DES.

The shape of Fe_3O_4@XAD-7 and its distribution in DES in colloidal gel were investigated by transformation electron microscopy (TEM) analysis. As shown in Figure 3(a and b), it was observed(image of DES), DES beads are dispersed in the form of an emulsion.

3 RESULTS AND DISCUSSIONS

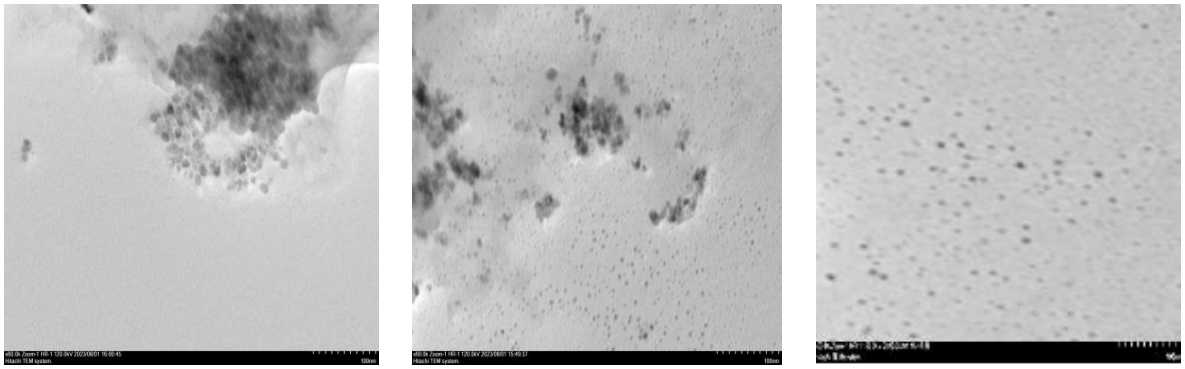
3.1 Effect of pH

pH is one of the most important parameters in the sorption of analyte onto the adsorbent. The increase or decrease of proton in the solution medium increases or decreases the affinity of the analyte to the adsorbent [16]. In order to determine the effect of pH on the recovery of Brown HT, the range of pH 2-8 was investigated. It is observed that the affinity of Brown HT to the adsorbent is high only at pH 4, from the acidic region to the basic region (pH 8). As shown in Figure 4, in this study, the sorption of Brown HT to nanoparticles was at maximum level at pH 4, the highest recovery was obtained at pH 4. Therefore, in the following experiments, the pH of the solutions was adjusted to 4.



a) b) c)

Figre 2. a) FT-IR spectrum of DES, b)Fe_3O_4@XAD-7 c) and Fe_3O_4@XAD-7/DES.



a) b) c)

Figure 3. a) TEM images of Fe3O4@XAD-7 b) and Fe3O4@XAD-7/DES c) DES.

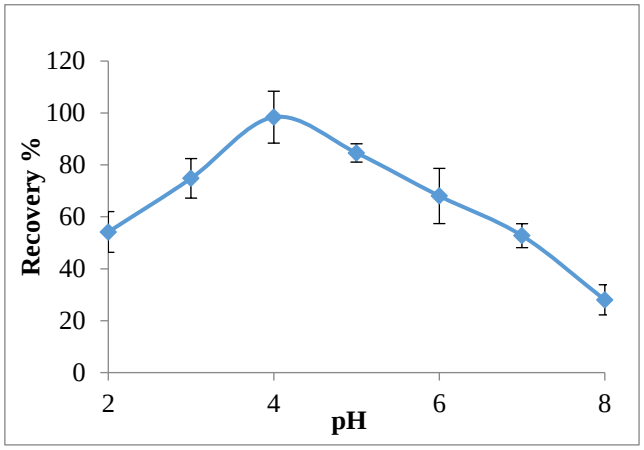


Figure 4. The effect of pH.

3.2 The Composition of Magnetic Colloidal Gel and Its Volume

In order to determine the optimum amount of nanoparticles in 1.0 mL of DES, the range of 20-80 mg was examined. The results obtained are presented in Figure 5. According to these results, the optimum amount of nanoparticles in 1.0 mL of DES should be 60 mg for the colloidal gel composition where the highest recovery is obtained. At values below 60 mg, the

recovery of Brown HT is quite low because the amount of nanoparticles is insufficient. Above 60 mg, there were no major changes in the recovery percentages.

After determining the composition of the colloidal gel, the volume of gel to be added to the solutions containing Brown HT must be determined. For this purpose, 100-600 µL of gel was added to the solutions. The results obtained are presented in Figure 6. According to these results, the optimum volume of gel to be added to the solutions is 400 µL. It was observed that the recovery of Brown HT increased continuously in the range of 100-400 µL of colloidal gel, and there were no major changes after 400 µL.

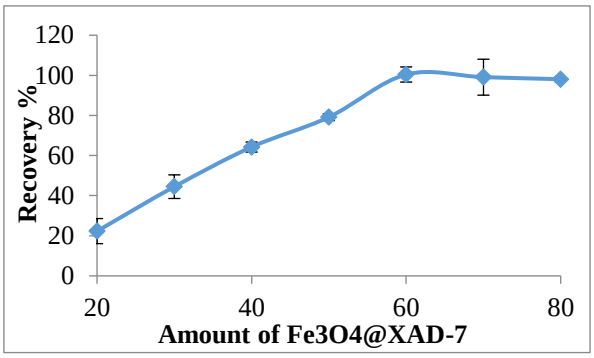


Figure 5. The effect of amount of Fe3O4@XAD-7.

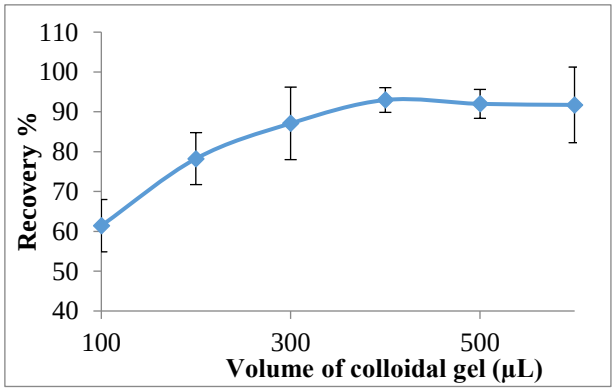


Figure 6. Effect of volume of colloidal gel.

3.3 Effect of Solvent Type

In this experiment, methanol, ethanol, acetonitrile, acetone and 0.1 M ammonia solutions of these solvents were used to investigate whether Brown HT completely passes into the solvent by reducing its interaction with the sorbent. As seen in Figure 7, it was determined that ammoniacal acetonitrile reduced the interaction between the sorbent and the analyte, thus recovering the analyte with high efficiency. Therefore, the best solvent was determined to be 0.1 M ammonia acetonitrile.

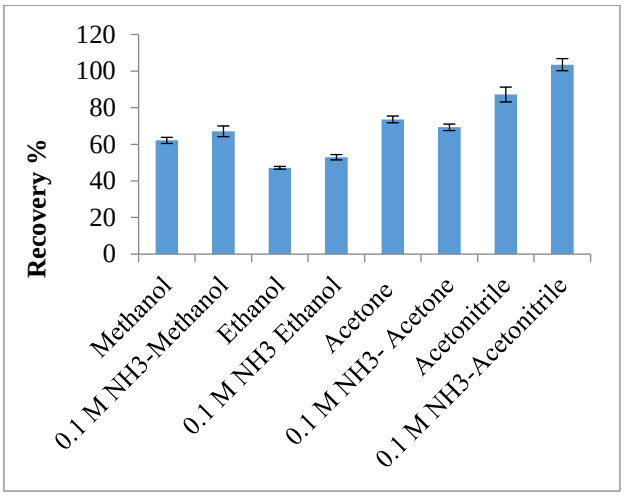


Figure 7. The effect of desorption solvent type.

3.4 Effect of Vortex Time

Vortex duration is a very important parameter in extraction studies. While it is important to increase the interaction between the analyte and the adsorbent in the adsorption process, it is important to increase the interaction between the extraction solvent and the analyte in the desorption process [17-18].

In the vortexing time study, Brown HT was investigated between 5-20 minutes for nanoparticle adsorption and 3-15 minutes for its desorption into ammonia acetonitrile solvent. It was determined that the most effective vortexing time in increasing the interaction between the nanoparticle and the analyte was 10 minutes, and the most effective vortexing time in transferring the analyte to the ammonia acetonitrile solvent was 8 minutes.

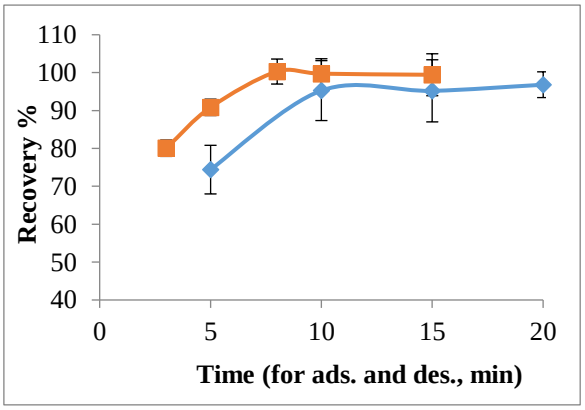


Figure 8. The effect of vortex time.

3.5 Sample Volume

To determine the highest sample volume at which the highest recovery was obtained, model solutions containing 0.5 $mg.L^{-1}$ Brown HT between 10-50 mL were examined. 10 mL and 20 mL were also mixed with 0.8 mL of ammoniacal acetonitrile, which is a high desorption solvent. The optimum sample volume was found to be 20 mL and the preconcentration factor was 25. All the results obtained are shown in Table 1.

Table 1. The effect of sample volume to extraction efficiency.

Sample volume (mL)	Recovery %
10	97.03
20	97.13
30	91.05
40	90.06
50	84.43

3.6 Matrix Effect

Under the determined optimum conditions, the selectivity of the sorbent to Brown HT was tested by matrix effect. For this purpose, the effects of ions abundant in drinking water and a commonly used food dye (amaranth) on the adsorption of Brown HT onto the sorbent were investigated. As seen in Table 2, As seen in Table 3, we can say that the selected ions and dye have no effect on the adsorption of Brown HT onto the sorbent at the concentrations examined in the matrix. With these results, we can say that the sensitivity of the method is high.

Table 2. The effect of interfering species to extraction efficiency.

Interfering species	Concentration (mgL^{-1})	Recovery %
K^+	3000	97
Mg^{2+}	250	97
Fe^{3+}	3	93
Cl^-	3000	97
Amaranth	0.5	99

3.7 Analytical Parameters of the Developed Method

According to the ICH-Q2 [19] validation procedures, the linear working range, detection and determination limits of the method were determined. Then, in the accuracy study, the analyte addition/recovery test was applied to real samples. Matrix effect study was applied for the selectivity of the method.

After determining the optimum condition of each parameter, the analytical performance of the method under these conditions was examined. First, it was determined in which working range of the method the relationship between the absorbance and concentration of Brown HT was linear. This range was determined to be 0.05-0.75 mg L^{-1} under optimum conditions. The correlation equation in this concentration range is A= 1.2354C-0.0127, with a correlation coefficient of 0.9962 (C: Brown HT Concentration (mgL^{-1}); A: Absorbance of Brown HT). In the method, limit of detection and quantification (LOD and LOQ) were calculated 0.016 mgL^{-1} and 0.052 mgL^{-1}, respectively. EF and PF of developed method were found to be 51, and 25, respectively. The analytical data of the method are given in Table 3.

LOD was calculated with the formula $3s_b/m$ where s_b and m are the standard deviation of the blank solution and the slope of the calibration curve, respectively. LOQ was calculated as 10 times s_b/m. EF was calculated by dividing the slopes of the calibration curves obtained before and after the preconcentration method. The RSD% of the developed method was calculated with the results obtained from 10 measurements of the lowest concentration in the working range [12].

Table 3. Analytical performance of the developed microextraction.

Parameters	Values
Linear equation	*A= 1.2354C -0.0127
R^2	0.9963
Linear range (mgL^{-1})	0.05-0.75
LOD (3 s/m) (mgL^{-1})	0.016
LOQ (10 s/m) (mgL^{-1})	0.052
RSD %	3.8
EF	51
PF	25

*C:Concantration of Brown HT (mgL^{-1}), A: Absorbance of Brown HT

3.8 Applying the Procedure to Real Samples

To determine the accuracy of the method, the analyt addition/recovery test was applied to real samples. For this purpose, Analyte was added to the chocolate sauce samples at 3 different concentrations to form 3 parallel solutions [15]. The developed method was applied to these prepared solutions. Then, the recoveries of Brown HT in the solutions were calculated. All the results obtained are shown in Table 4. The total Brown HT content in the sample is presented in Table 5. The developed method was successfully applied to chocolate sauce as a

real sample and the result found was below the maximum level of 50 $mg.kg^{-1}$ determined by the Turkish Food Codex [20].

For the precision of the method, repeatability (intraday) and intermediate precision (interday) tests were applied to 3 parallel solutions of the analyte at 2 different concentrations. For intraday study, the method was applied to the solutions at 3 different times in one day, and in the interday study, the method was applied to the solutions on 3 different consecutive days.

The results of intraday and interday studies were evaluated by calculating RSD% (Table 6). While RSDs % were in the range of 1.2-2.4% in the intraday study, RSDs % were in the range of 4.3-6.1% in the interday study. According to the ICH-Q2 evaluation, precision results are evaluated with % RSDs. Accordingly, if the RSDs % are below 10, the precision of the method can be considered high.

Table 4. Application of the procedure to real samples(N=3).

Sample	Added, mgL^{-1}	Found, mgL^{-1}	Recovery %
Chocolate sauce	0.10	0.28	98±2
	0.25	0.443	104±3
	0.50	0.678	99±5

Table 5. Content of Brown HT in the chocolate sauce(N=3).

$mg.kg^{-1}$±1.4

Table 6. The repeatability (intraday) and intermediate precision (interday) of the method, N=3.

		Intraday			Interday		
	Added (mgL^{-1})	Found (mgL^{-1})	Recovery %	RSD %	Found (mgL^{-1})	Recoveryy %	RSD %
Chocolate sauce	-	0.21	-	1.2	0.19	-	4.3
	0.2	0.42	105	2.4	0.41	110	6.1
	0.4	0.59	95	1.8	0.60	103	4.4

3.9 The Comparison Between the Developed Method and Other Techniques Reported in the Literature

According to our research, there are very few studies in the literature on the determination of Brown HT. The LOD of the method we developed is quite low compared to the Cloud Point Extraction method in Table 7, while the PF is high. The linear range is quite wide compared to the DES based microextraction method developed with UV-Vis spectrophotometer.

The advantage of this study is that it provides an up-to-date, simple, environmentally friendly, sensitive and accurate method due to the scarcity of studies on the determination of Brown HT. Magnetic nanoparticles were easily removed from the medium with an external magnet.

Therefore, no extra process was required to remove the particles. It will shed light on this dye to researchers with an up-to-date method.

Tablo 7. The comparison between the suggested method and other techniques reported in the literature.

Method	Enstrument	Real Sample	LOD (mgL^{-1})	PF	Linear Range (mgL^{-1})	Ref.
Direct differential pulse polarography	Saturated calomel electrode	Orange, lime, blackcurrant drinks	-	-	0-45.5	[21]
Cloud point extraction	Scanometry	Water	0.04	19.05	0.06–2.60	[9]
Deep eutectic solvent based microextraction	UV-Vis	Cake, two different urines, two different water	0.23	37.5	0.23–1.04	[10]
MCG- dSPME	UV-Vis	Chocolate sauce	0.016	25	0.05-0.75	This work

*UV-Vis: Ultraviyole spectrophotometry; MCG-dSPME: magnetic colloidal gel based dispersive solid phase microextraction

4 CONCLUSION

A new magnetic colloidal gel based dispersive solid phase microextraction method (MCG-dSPME) was developed for the preconcentration of Brown HT. This colloidal gel was obtained by mixing Fe_3O_4@XAD-7 and DES (choline chloride/phenol; 1/2). In this developed method, LOD, PF, EF values were calculated as 0.016 mg L^{-1}, 25, 51, respectively. The working range of Brown HT was found as 0.05-0.75 mg L^{-1} in this method. The linear range of our method is wide, LOD is low, selectivity, accuracy and precision are high. The low LOD and

high selectivity, EF and PF of our method enable the determination of Brown HT, even at trace levels, in many complex matrices.

The developed method was successfully applied to chocolate sauce as a real sample and the result found was below the maximum level of 50 $mg.kg^{-1}$ determined by the Turkish Food Codex [20].

Studies on the determination of this dye are quite few in the literature. The magnetic colloidal gel based dispersive solid phase microextraction method developed for the determination of Brown HT has great importance in this respect.

Statement of Research and Publication Ethics

The study is complied with research and publication ethics.

Artificial Intelligence (AI) Contribution Statement

This manuscript was entirely written, edited, analyzed, and prepared without the assistance of any artificial intelligence (AI) tools. All content, including text, data analysis, and figures, was solely generated by the authors.

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