



Determination of trace amounts of Brown HT as a food dye by a CPE-scanometry method

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Abstract

In this study, trace amounts of Brown HT were extracted, pre-concentrated and determined by cloud point extraction-scanometry (CPE-scanometry) as a simple, fast and inexpensive method. The procedure is based on CPE of Brown HT from an aqueous solution, diluting the extracted surfactant-rich phase with ethanol to 500 μL , transferring the appropriate volume to Plexiglas® cells and scanning the cells. Then, the colour of each cell was analyzed by software written in visual basic (VB 6) into red, green and blue values. Effective parameters for the extraction efficiency, such as the pH of the system, the concentration of surfactant, the equilibration temperature and equilibration time, were investigated and optimized. Under optimal conditions, the calibration curve was linear in the range of 0.06–2.60 mg L^{-1} . The detection limit of the proposed method was 0.04 mg L^{-1} . In addition, the effects of some foreign species, including cations, anions and dyes, were investigated. The method was applied successfully for the determination of Brown HT in some water samples.

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Keywords: Brown HT; CPE-scanometry; Food dye

1. Introduction

Brown HT (Fig. 1) is the disodium salt of 4,4'-(2,4-dihydroxy-5-hydroxymethyl)-m-phenylene)-bis(azo)]-di-1-naphthalene-sulphonic acid. There are at least 10 synonyms for this compound. The most

commonly used synonyms in published literature are Brown HT, Chocolate Brown HT and CI Food Brown 3 [1]. It presents very good stability in light and heat [2].

Brown HT is permitted for use in the UK under the Colouring Matter in Food Regulations, and its review by the EEC authorities is pending. The principal uses of Chocolate Brown HT are in flour and sugar confectionery, canned meat, ice cream, soft drinks, puddings and sauces [3]. Toxic effects have been observed from high concentration Brown HT, including brown colouration of internal organs [4] and decreased levels of norepinephrine, dopamine and gamma-aminobutyric acid in all tested regions [5].

Cloud point extraction (CPE) is a unique extraction method that provides cost effective sample preparation

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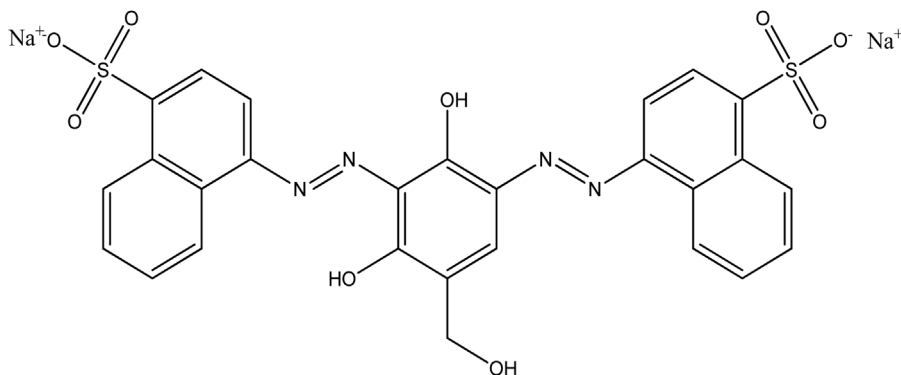


Fig. 1. Molecular structure of Brown HT.

with a high extraction efficiency [6–13]. This separation method is based on the temperature-dependent aggregation behaviour of surfactants in aqueous solution. If a solution with a surfactant concentration above the critical micellar concentration (c.m.c.) is heated to a certain temperature, termed the cloud point, the surfactant molecules form micelles that generate an additional phase. This surfactant-rich phase, depending on the type of surfactant employed, is lighter or heavier than the aqueous phase and can easily be separated from the latter.

Non-polar molecules are able to enter micelles and are therefore co-extracted, while polar substances and ions will remain in the aqueous phase [14]. In this manner, CPE using non-ionic surfactants has attracted considerable attention as an alternative to conventional extraction methods for separation and pre-concentration [15–17].

The cloud point extraction method has been successfully employed for the pre-concentration of compounds, such as food samples [18–20], environmental samples [8,21], biological samples [21,22], dyes [13,23–25], biomaterials [26] and pharmaceuticals [27,28].

Auxiliary methods, such as ultrasonic-assisted cloud point extraction (UA-CPE) [29], microwave-assisted cloud point extraction (MA-CPE) [30], CPE-SPE [31], CPE assisted by nanoparticles [32], and stirring-assisted cloud point extraction (SA-CPE) [33], are also applicable. CPE has been shown to be an effective procedure for analyte extraction, pre-concentration and purification that improves the sensitivity, selectivity, detection limit and other analytical characteristics prior to HPLC [34], GC [35], CE [36,37], spectroscopy [38,39], inductively coupled plasma (ICP) [40], atomic absorption spectrometry [41,42], spectrophotometry [43], HPLC–UV [13], aptode [25] and solution scanometry [44–46].

The scanometry method was introduced recently by Abbaspour et al. [47]. They used commercially available flatbed scanners to obtain images of coloured solutions. The obtained images were transferred to a computer to

analyze the coloured solutions and determine their intensity. The method is based on the reaction in solution phase in Plexiglas® cells. The solution was scanned, and ultimately, the RGB (red, green and blue) colour model was used in a colour monitor [48,49].

Recently, CPE has been coupled with scanometry into CPE-scanometry and used for the pre-concentration and determination of fast green FCF as a food dye [50] and Violet Covasol as a cosmetic dye [51]. This method has several benefits, including inexpensiveness, short response time, system portability, easy immobilization of reactants, simplicity, high scanning speed, no need to determine λ_{\max} , intense archiving of experiences, and limited interference from reflective properties of the surface.

Given the importance of the benefits and disadvantages of Brown HT, the measurement of it appears to be necessary. A few methods for the determination of Brown HT have been described in the published literature, of which variations of high pressure liquid chromatography (HPLC) appear to be the most generally employed [52]. Therefore, the development of a simple sensitive and accurate method for the analysis of Brown HT is important. The main goal of this study is the pre-concentration and determination of trace amounts of Brown HT dye. CPE-scanometry is a new method for this purpose.

2. Experimental

2.1. Apparatus

Cells (a 1000 μL volume each) were built by using a sheet of Plexiglas®. A Canoscan LiDE 200 flatbed scanner was used for scanning the Plexiglas® sheet. The resolution of the scanner was regulated at 300 dpi. VB based special software [32] was used to convert the recorded colour pictures of the cells to RGB data. Biohit

proline pipettors, 0.5–10, 10–100 and 100–1000 μL , were used to inject samples into the cells. A Metrohm (Herisau, Switzerland) digital pH metre Model 827 with a combined glass electrode was used to measure the pH values. An A. F.A.G. thermostat bath (Iran) maintained at the desired temperature was used for the cloud point temperature experiments. A RHB model centrifuge (Germany) was used for the cloud point methodology.

2.2. Materials

All solutions were prepared with deionized water. A 1% (w/v) Triton X-114 (Fluka, Buchs, Switzerland) solution was prepared by dissolving 1.0 g of Triton X-114 in a 100-mL volumetric flask. Brown HT (disodium salt of 4,4'-[(2,4-dihydroxy-5-hydroxymethyl)-m-phenylene]bis(azo)]-di-1-naphthalene-sulphonic acid) was purchased from Neelikon company. Carmine and thymolphthalein were purchased from Merck Company. A stock solution of 200 mg L^{-1} of Brown HT was prepared by dissolving the proper amount of Brown HT in water and diluting it to 100 mL in a volumetric flask, and more diluted solutions were prepared from this solution. Nitrate salts of sodium, cobalt, nickel, magnesium, potassium, cadmium, calcium, lithium, copper and others from Merck Company were of the highest purity available and used without any further purification. The adjustment of pH for optimum conditions was performed by the addition of an acetate/acetic acid buffer solution. The surfactant rich phase was diluted with ethanol.

2.3. Principles of the red, green and blue (RGB) colour system

The RGB colour model is an additive colour model in which red, green, and blue light are added together in various ways to reproduce a broad array of colours. In computing, colour values are often stored as integer numbers in the range 0–255, the range that a single 8-bit byte can offer (by encoding 256 distinct values). In the RGB system, any colour is represented in the form of (R, G, B), in which (0, 0, 0) and (255, 255, 255) refer to black and white, respectively. Therefore, by increasing the intensity of colours, the colour values are decreased. In this system, 16,777,216 colours can be made. Any colour can be described by the following formula:

$$V = R + 256G + 2562B$$

where R , G and B are the red, green and blue values of the main colour, respectively. For black and white, V is equal to 0 and 16,777,216, respectively. By using the

following flowchart, the R , G and B values of V for any colour can be extracted:

$$R = V \text{ Mod } 256$$

$$G = \frac{((V - R) \text{ Mod } (256^2))}{256}$$

$$B = \frac{V - R - G * 256}{256^2}$$

“Mod” is a numeric function that returns the remainder when dividing two numbers.

2.4. Procedure

A typical cloud point experiment was carried out using the following procedure. An aliquot of 15 mL of an aqueous solution containing 2 mg L^{-1} of Brown HT and 0.16% (w/v) Triton X-114 at pH 4 (adjustment by adding $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ buffer) was prepared. Then, the mixture was heated for 20 min in a thermostatic bath at 45 °C. The two phases that formed were separated by centrifuging for 5 min. The surfactant-rich phase became viscous and was retained at the bottom of the tube, while the bulk aqueous phase was carefully removed by Pasteur pipette. The surfactant-rich phase was diluted with ethanol to 500 μL , and 450 μL of this solution was injected into one cell on a Plexiglas® sheet, as was done for the other cells. After shaking, the colour cells were scanned with the scanner, and the obtained images of the coloured solutions were analysed to evaluate the R , G and B contents by the developed software. In scanometry, unlike spectrophotometry, the reflection of coloured solutions is studied; therefore, an R , G or B value of a coloured solution that has the same colour as the solution is usually useless because this value is often higher than 167.00 and does not significantly change during the experiment. In this study, because B values were more sensitive (higher slope) to increases of the Brown HT concentration, this parameter was chosen as the basic parameter. Any effective intensity in colour value (R , G and B) between the sample solution and blank was plotted vs. the considerable parameter.

$$\text{Effective intensity}_R = -\log\left(\frac{R_{\text{sample}}}{R_{\text{blank}}}\right)$$

$$\text{Effective intensity}_G = -\log\left(\frac{G_{\text{sample}}}{G_{\text{blank}}}\right)$$

$$\text{Effective intensity}_B = -\log\left(\frac{B_{\text{sample}}}{B_{\text{blank}}}\right)$$

In the experiments, the value varied between 86.74 and 148.0 for the *B* parameter relative to the Brown HT concentration.

2.5. Preparation of real samples

Real samples, including tap water (Esfahan city) and mineral water (Koohrang and Dasani), were used without any preliminary preparation. Samples in the amount of 5 mL were taken and measured according to the method mentioned in the procedure section.

3. Results and discussion

A method for the pre-concentration and determination of Brown HT was developed using CPE-scanometry. The RGB parameters of Brown HT were recorded after CPE with Triton X-114. The *B* parameter for 2 mg L⁻¹ of Brown HT was found to be the most sensitive signal without and with cloud point extraction (0.01 and 0.25, respectively); thus, this method can be used as a sensitive method. Various experimental parameters, such as the pH of the medium, the Triton X-114 concentration, the temperature, the time in the bath and the centrifuge time were studied to obtain an optimized system. These parameters were optimized by the one-at-a-time evaluation method.

3.1. Effect of pH

For the Brown HT molecule, because of the presence azo, hydroxyl, and sulfonate groups, which have different powers for accepting, the proton pH had great ability to extract the micellar phase. Therefore, the influence of pH on the CPE was evaluated (Fig. 2). The

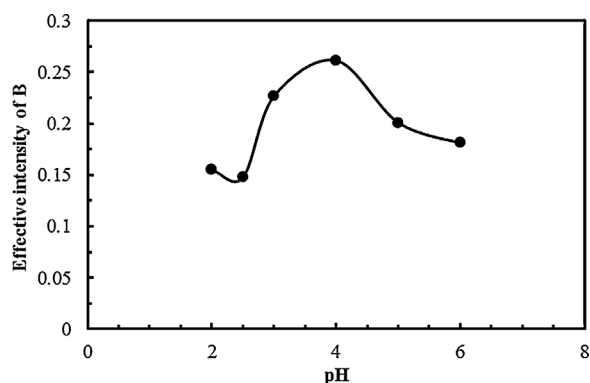


Fig. 2. Effect of pH of the test solution on the CPE of Brown HT (conditions: Brown HT, 2 mg L⁻¹; Triton X-114, 0.16% (w/v); temperature of bath, 45 °C).

effect of pH on the CPE of 2 mg L⁻¹ of Brown HT was studied in the range of 2–6 by the addition of hydrochloric acid or sodium hydroxide. Fig. 2 shows that, at pH 4, the maximum colour intensity can be obtained. At low pH, the anionic group—SO₃⁻ changes to the uncharged group—SO₃H; therefore, the neutral form of Brown HT transfers to the surfactant phase and the extraction efficiency increases. In extremely acidic pH, neutral dye molecules become cationic by accepting H⁺, and therefore, recovery is reduced. At pH > 4, especially in alkaline solutions, the anionic form is mostly present, which causes a reduction in the extraction efficiency. Therefore, pH 4 was selected as the optimum pH value and was maintained by adding 2.5 mL of acetic acid/sodium acetate buffer solution.

3.2. Effect of Triton X-114 concentration

For a successful CPE, it is desirable to obtain minimum amounts of surfactant, which is required for the maximum extraction of dye. Therefore, the effect of the Triton X-114 concentration on the extraction of Brown HT was studied in the range of 0.06–0.23% (w/v). According to Fig. 3, the highest signal was obtained at 0.16% (w/v) of surfactant. At lower surfactant concentrations, the recovery is reduced because of the incomplete recovery of the extraction. The decreased signal at concentrations higher than 0.16% (w/v) is due to some amounts of Triton X-114 and analyte remaining in the aqueous solution. Therefore, this phase can compete with the surfactant-rich phase to draw dye into itself. Additionally, at high concentrations of surfactant, the viscosity of the enrichment phase was increased and the signal was decreased. Therefore, to obtain optimum

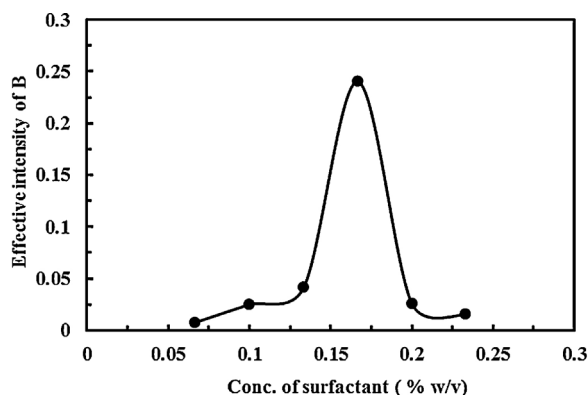


Fig. 3. Effect of the Triton X-114 concentration on the CPE of Brown HT (conditions: Brown HT, 2 mg L⁻¹; pH 4; temperature of bath, 45 °C).

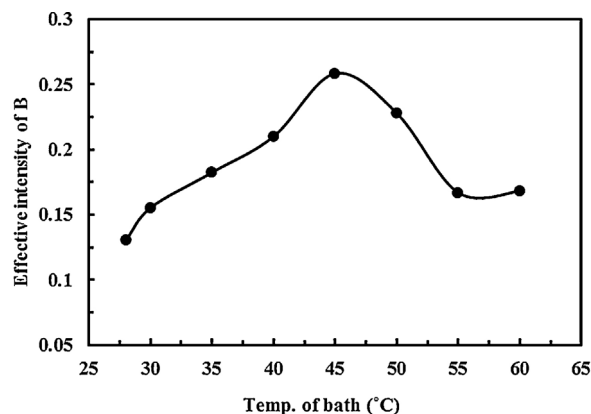


Fig. 4. Effect of the equilibration temperature on the CPE of Brown HT (conditions: Brown HT, 2 mg L^{-1} ; Triton X-114, 0.16% (w/v); pH, 4; temperature of bath, 45°C).

conditions, a 0.16% (w/v) solution of Triton X-114 concentration was selected for further studies.

3.3. Effects of equilibration temperature and time

It is known that two phases are formed when the temperature increases; dehydration occurs and decreases the volume of the surfactant-rich phase and increases the phase–volume ratio.

At the higher temperature of the cloud point phenomenon, two phases are created, including an aqueous and a surfactant-rich phase, and at lower temperatures, these two phases cannot be formed. Additionally, at excessive temperatures, surfactant-dye dissociation occurs and the decomposition of the analyte may follow. Thus, it is necessary to optimize temperature as an important factor to achieve easy separation, pre-concentration, and complete extraction. Therefore, the effect of the equilibrium temperature in the range of $28\text{--}60^\circ\text{C}$ was studied. As shown in Fig. 4, the extraction efficiency reached its maximum at 45°C . Additionally, the time of equilibration has an important role in achieving a suitable extraction because of the same effect of temperature; therefore, it seems to be necessary to optimize this factor. The dependence of the extraction efficiency on the equilibration time was studied for a time interval of 7–30 min. According to Fig. 5, the maximum extraction efficiency was observed at 20 min.

3.4. Effect of centrifugation time

It is required to pre-concentrate trace amounts of Brown HT with high efficiency in a short time. The effect of the centrifugation time on phase separation was studied in the range of 2–25 min. The result showed that

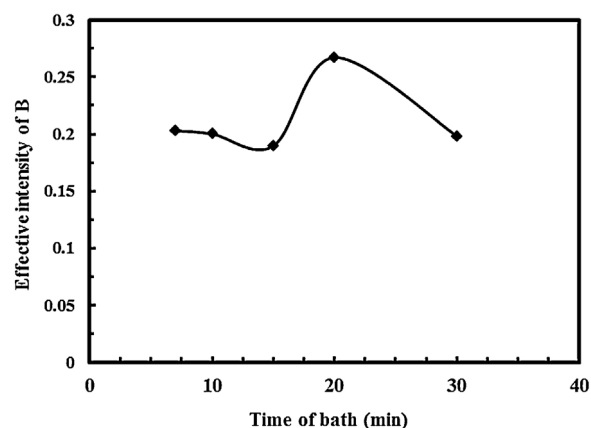


Fig. 5. Effect of the equilibration time on the CPE of Brown HT (conditions: Brown HT, 2 mg L^{-1} ; Triton X-114, 0.16% (w/v); pH, 4; temperature of bath, 45°C).

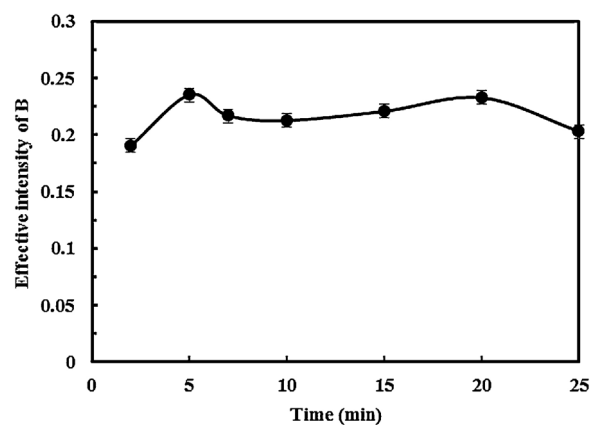


Fig. 6. Effect of the centrifugation time on the CPE of Brown HT (conditions: Brown HT, 2 mg L^{-1} ; Triton X-114, 0.16% (w/v); pH, 4; temperature of bath, 45°C).

the best separation was obtained with a centrifugation time of 5 min (Fig. 6); at shorter times, the separation was not complete, and at longer centrifugation times, considerable changes in signal were not observed.

3.5. Effect of the salt concentration

The CP of a micellar solution can be controlled by the addition of a salt (salting-out effect), alcohol, non-ionic surfactant or some inorganic and organic compounds. It had been reported [9,24] that the addition of salt to the solution may influence the extraction process. To study the effect of salt addition on micellar solutions of Brown HT, a KCl solution was tested. It was observed that the addition of KCl up to 0.1 mol L^{-1} had no significant effect on the CPE efficiency.

Table 1
Investigation of the interference effects of several species on the determination of 1 mg L⁻¹ Brown HT by CPE-scanometry.

Foreign ion/dye	Tolerable limits of interference (mg L ⁻¹)
Na ⁺ , Co ²⁺ , Ni ²⁺ , Mg ²⁺ , Cd ²⁺ , K ⁺	1000
SO ₄ ²⁻ , HCO ₃ ⁻ , PO ₄ ³⁻ , Cl ⁻	1000
ClO ₄ ⁻	750
Ca ²⁺ , Li ⁺	100
Pb ²⁺	50
Cu ²⁺	5
Carmines	1
Thymolphthalein	1

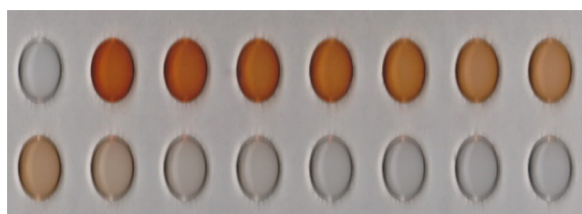


Fig. 7. Scanning image of Brown HT at different concentrations (0.006–6.000 mg L⁻¹).

3.6. Effect of foreign species

The influence of some diverse cations, anions and dyes on the determination of Brown HT were studied. The interfering capacity of water matrix constituents, such as calcium, magnesium, sodium, sulphate and other ions, and non-ionic species on recovery was also considered. Various amounts of other species were added to a solution containing 1 mg L⁻¹ of Brown HT, and the recommended procedure under optimum conditions was applied. An error of less than or equal to 5.0% in the signal reading was considered a tolerable value (Table 1).

3.7. Analytical figures of merit

Under optimum conditions, different solutions of analytes with concentrations in the range of 0.006–6.000 mg L⁻¹ were scanned; the images (Fig. 7) were analyzed and a linear range of 0.06–2.60 mg L⁻¹ of Brown HT was obtained (Fig. 8). As the *R* and *G* values do not vary considerably by changing the concentration of dye, RSD values were calculated only for *B* values.

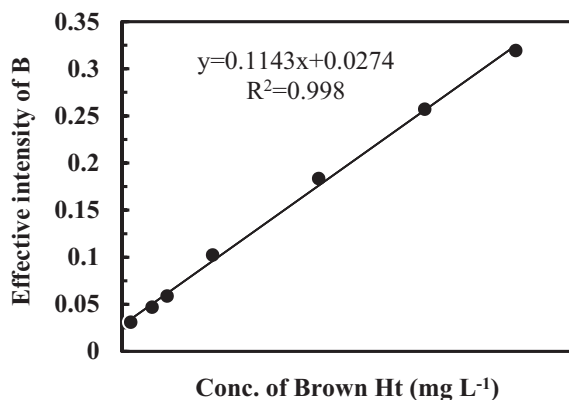


Fig. 8. Calibration curve for the determination of Brown HT by CPE-scanometry.

The equations for the regression line with and without the pre-concentration were $(EI)_B = 0.1143C + 0.0274$ and $(EI)_B = 0.006C - 0.0017$, respectively, where $(EI)_B$ and *C* are the effective intensity *B* parameter and the concentration of Brown HT in mg L⁻¹, respectively. The detection limit based on five times the standard deviation of the blank ($3S_b$) for the *B* factor was found to be 0.04 (*n* = 5). The relative standard deviation (RSD) for 2 mg L⁻¹ of Brown HT was 1.10 for *B* (*n* = 5). The enrichment factor, defined as the ratio of the calibration curve's slope with and without pre-concentration, was 19.05 for the proposed method. The pre-concentration factor based on the ratio of the initial volume in the centrifuge tube to the final volume of the dissolving solvent was 30.

3.8. Application to real samples

The proposed method was validated for the analysis of Brown HT in water samples, including tap (Esfahan city) and mineral water, using Koohrang and Dasani under optimum conditions. The corresponding scanning images are shown in Fig. 9. The concentration of this dye in the cited real samples was calculated from standard addition calibration curves. For the other water samples, the developed methodology was validated by recovery studies. Additionally, the developed methodology was validated by recovery studies. Good recovery

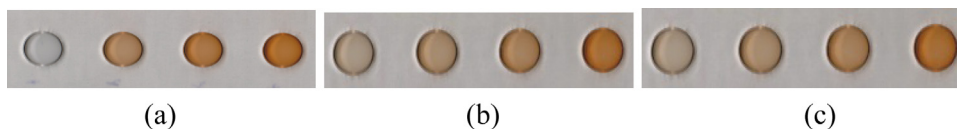


Fig. 9. Scanning images of real samples: tap water (a), mineral water including Koohrang (b) and Dasani (c).

Table 2
Measurement of Brown HT dye in water samples by CPE-scanometry.

Sample	Regression equation	R^2	Added (mg L^{-1})	Found (mg L^{-1})	Recovery %
Mineral water (Dasani)	$(EI)_B = 0.1198C + 0.0076$	0.9955	00.00	Nd ^a	
			0.33	0.34	103.15
			0.66	0.62	94.48
Mineral water (Koohrang)	$(EI)_B = 0.1362C + 0.0068$	0.9631	00.00	Nd	
			0.33	0.39	108.02
			0.66	0.60	91.58
Tap water (Esfahan city)	$(EI)_B = 0.1683C - 0.017$	0.9924	00.00	Nd	
			0.33	0.34	105.70
			0.66	0.70	106.60

^a Not detected.

(91.57–108.02%) was achieved for all analyzed samples. The results of this study are presented in Table 2.

4. Conclusions

The trace amounts of Brown HT as a food dye [43] determined by CPE-scanometry show that it is an easy, safe, rapid, portable, and inexpensive method for the separation, pre-concentration and determination of trace amounts of dyes with higher pre-concentrations and good enrichment factors for aqueous solutions. The analytical results showed that the developed method can be successfully adopted for the separation and determination of dyes with good sensitivity and selectivity, despite the fact that in published reports there are no figures on its merit or quantitative value [1]. The linear range of the proposed method for the determination of Brown HT is relatively wide. The proposed method can be applied for the pre-concentration and determination of Brown HT in various water samples.

Conflict of interest

None declared.

Acknowledgement

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