Food Chemistry 141 (2013) 182–186

Contents lists available at SciVerse ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

A rapid shaking-based ionic liquid dispersive liquid phase microextraction for the simultaneous determination of six synthetic food colourants in soft drinks, sugar- and gelatin-based confectionery by high-performance liquid chromatography

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ARTICLE INFO

Article history:
Received 8 February 2012
Received in revised form 2 March 2013
Accepted 5 March 2013
Available online 14 March 2013

Keywords:
Rapid shaking-based ionic liquid dispersive liquid phase microextraction
Synthetic food colourants
High-performance liquid chromatography

ABSTRACT

A novel and simple rapid shaking-based method of ionic liquid dispersive liquid phase microextraction for the determination of six synthetic food colourants (Tartrazine, Amaranth, Sunset Yellow, Allura Red, Ponceau 4R, and Erythrosine) in soft drinks, sugar- and gelatin-based confectionery was established. High-performance liquid chromatography coupled with an ultraviolet detector was used for the determinations. The extraction procedure did not require a dispersive solvent, heat, ultrasonication, or additional chemical reagents. 1-Octyl-3-methylimidazolium tetrafluoroborate ($[C_8MIM][BF_4]$) was dispersed in an aqueous sample solution as fine droplets by manual shaking, enabling the easier migration of analytes into the ionic liquid phase. Factors such as the $[C_8MIM][BF_4]$ volume, sample pH, extraction time, and centrifugation time were investigated. Under the optimum experimental conditions, the proposed method showed excellent detection sensitivity with limits of detection (signal-to-noise ratio = 3) within 0.015–0.32 ng/mL. The method was also successfully used in analysing real food samples. Good spiked recoveries from 95.8%–104.5% were obtained.

1. Introduction

Colour is a main feature of foods. Its affect on people is not only visual; it is also associated with food variety, quality, and freshness. Food colourants have been used to replace natural food colour, which can be lost during preparation processes. Colourants are also used to prevent colour changes in the final product (Berzas, Flores, Llerena, & Farinas, 1999) and provide attractiveness to consumers, particularly children (Hofer & Jenewein, 1997). In recent years, natural food colourants isolated from suitable plants, fungi, or insects have been increasingly used. However, many natural colourants become unstable under processing conditions such as, light, oxygen, and pH. Natural colourants are also more expensive than synthetic ones. The use of synthetic organic dyes has been recognised as the most reliable and economical method of restoring or providing colour to a processed product. However, some of these substances pose potential risks to human health, especially when consumed in excess.

To prevent indiscriminate use, laws and regulations based in toxicological studies on experimental animals and human clinical studies have been developed in many countries. The policies limit the types, purities, uses, and amounts of food colourants permitted in food and drinks. Consequently, sensitive, accurate, and reliable methods for determining synthetic colourants are required to ensure food safety.

Several analytical techniques have been developed to facilitate the simultaneous determination of various synthetic food colourants. Such techniques include derivative spectrometry and other spectrophotometric methods related with chemometrics (Al-Degs, 2009; Berzas et al., 1999; Ni & Gong, 1997; Sayar & Özdemir, 1998), adsorptive voltammetry (Ni, Bai, & Jin, 1997), differential pulse polarography (Chanlon, Joly-Pottuz, Chatelut, Vittori, & Cretier, 2005; Combeau, Chatelut, & Vittori, 2002), thin-layer chromatography (Morlock & Oellig, 2009), capillary electrophoresis (Dossi et al., 2007; Ryvolova, Taborsky, Vrabel, Krasensky, & Preisler, 2007), high-performance liquid chromatography (HPLC) (Minioti, Sakellariou, & Thomaidis, 2007; Pereira Alves, Brum, Branco de Andrade, & Pereira Netto, 2008; Vidotti, Costa, & Oliveira, 2006; Yoshioka & Ichihashi, 2008), as well as ion chromatography (Chen, Mou, Hou, Riviello, & Ni, 1998).

A recently proposed method, dispersive liquid–liquid microextraction (DLLME) (Rezaee et al., 2006), is based on the formation of a turbid solution by the rapid injection of a mixture containing

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http://dx.doi.org/10.1016/j.foodchem.2013.03.015

extraction and disperser solvents into an aqueous solution. The extraction solvent is dispersed into the aqueous sample as very fine droplets, enabling the analytes to transfer easily to the extraction solvent. When extraction equilibrium is achieved, phase separation is performed by centrifugation and the enriched analytes in the sediment phase can be determined. Compared with other microextraction methods, this technique is more convenient, simple, and requires less expensive devices. More importantly, DLLME can be applied under batch conditions and extraction can be completed in several seconds, resulting in faster extraction and shorter analytical time.

Room temperature ionic liquids (RTILs) are a group of new organic salts consisting of organic cations and various anions that are liquid at room temperature. RTILs have been used as extraction solvents in place of organic solvents because of their unique physicochemical properties, such as negligible vapour pressure, miscibility with water and organic solvents, good solubility in organic and inorganic compounds, and high thermal stability as well as being environmentally benign (Pandey, 2006; Poole & Poole, 2010). DLLME based on ion liquids (ILs) (IL-DLLME) was introduced by Zhou et al. in 2008 (Zhou, Bai, Xie, & Xiao, 2008). This approach needs an organic solvent as the dispersive solvent and heat to aid the complete dispersion of a water-immiscible IL into the aqueous phase, then sedimentation by cooling with ice water. Extraction requires a specific heating time and cooling process, which is relatively time and energy consuming. To improve the extraction performance of temperature-controlled DLLME, ultrasound is used to disperse the IL extraction solvent (Zhou, Zhang, & Xiao, 2009), but the cooling process and dispersive organic solvent are still needed to obtain a turbid solution. Then Yao and Anderson (2009) reported a method for in situ IL formation DLLME, wherein the hydrophilic IL is completely dissolved in the aqueous phase and an ion-exchange reagent is added to form a water-immiscible IL. Although this method overcomes the weaknesses described above, the addition of excess ion-exchange reagent is required, which complicates the method.

In the current work, a simple and efficient manual shaking-based method of IL-DLLME was developed. The procedure does not require a dispersive solvent, heat, ultrasonication, or additional chemical reagents, in contrast to conventional IL-DLLME. IL ($[C_8MIM][BF_4]$) was dispersed in an aqueous solution as fine droplets by manual shaking, promoting migration of the analytes to the ionic liquid phase, then coupled with HPLC-ultraviolet (UV) spectrophotometry determination. The effects of various experimental parameters, including the $[C_8MIM][BF_4]$ volume, sample pH, extraction time, and centrifugation time, have been investigated and optimised for the extraction of six synthetic food colourants.

2. Materials and methods

2.1. Reagents and standards

The standard stock solutions of the colourants Tartrazine (TAR; C.I. Food Yellow 4; 0.5 mg/mL), Amaranth (AMA; C.I. Food Red 9; 0.5 mg/mL), Sunset Yellow (SUN; C.I. Food Yellow 3; 0.5 mg/mL), Allura Red (ALL; C.I. Food Red 17; 1.0 mg/mL), Ponceau 4R (PON; C.I. Food Red 7; 0.5 mg/mL), and Erythrosine (ERY; C.I. Food Red 14; 0.1 mg/mL) were obtained from the National Research Center for Certified Reference Materials (Beijing, China). The mixed standard solutions containing all colourants at 0.05 mg/mL was prepared by mixing and dilution of appropriate aliquots from standard stock solution of each substance. Working solutions were prepared by appropriate dilutions of the mixed standard solutions with water.

HPLC-grade methanol and acetonitrile were purchased from Tianjin Guangfu Fine Chemical Research Institute (Tianjin, China). 1-Octyl-3-methylimidazolium tetrafluoroborate ($[C_8MIM][BF_4]$), 1-hexyl-3-methylimidazolium chloride ($[C_6MIM][Cl]$), and 1-octyl-3-methylimidazolium chloride ($[C_8MIM][Cl]$) were obtained from Shanghai Cheng Jie Chemical Co., Ltd. (Shanghai, China). Milli-Q water (Millipore, Bedford, MA, USA) was used throughout the study. All other reagents were analytical grade and were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). All solutions prepared for HPLC were filtered through 0.45 μm membranes before use.

2.2. Instruments

The chromatography equipment was a 1525 binary HPLC pump and a 2489 dual λ UV detector from Waters (Waters Corporation, USA). The Waters Breeze software was used to control the instruments and acquire data. The chromatographic separation of the analytes was carried out on a Gemini C18 column (5 μm; 4.6 mm × 250 mm; Phenomenex, Torrance, CA, USA). A pH meter (Model pHS-3C, Shanghai Tianda Apparatus Co., Ltd., China) was used for pH adjustment. A centrifuge Model TDZ4-WS (XiangYi Centrifuge Instrument Co., Ltd., China) was employed to accelerate the phase-separation process.

2.3. Preparation of the sample solution

All samples, including soft drink, sugar-based and gelatin-based confectionery, were obtained from a local market. Appropriate amounts (0.3–2.5 g) of the samples were dissolved in 25 mL of water. The carbonated drinks were degassed by ultrasonication for 5 min. A warming process (50 °C, 30 min) was used for the complete dissolution of the sugar-based and gelatin-based confectionery. Samples were diluted to 50 mL in a volumetric flask with an acetate buffer solution (0.2 mol/L, pH 5.0). These solutions were filtered through a folded Xinhua paper filter (No. 102), and the filtrate was collected after discarding the first 15 mL.

2.4. Extraction procedure

A homogeneous sample solution (10.0 mL) containing the analytes was placed in a 15 mL screw-cap conical-bottom graduated plastic centrifugal tube. Using a 500 μL syringe, 350 μL of RTIL was injected into the sample solution. Manual shaking (30 times in 20 s) resulted in the formation of a turbid solution, which was centrifuged for 8 min at a rate of 3500 rpm (1685*g*). The upper aqueous solution was removed using a pipette, and the volume of residual IL was almost 180 μL. Methanol was added to the IL residue enriched with analytes to obtain a volume of 300 μL. Using a 25 μL HPLC microsyringe, 10 μL of the enriched solution was injected directly into the HPLC system. All experiments were performed in triplicate. The syringe was rinsed with methanol and acetonitrile multiple times to remove residual analytes and IL.

2.5. Interference experiments

The interferences were studied by analysing 10 mL solution containing 100 ng mL^{-1} colourants and other chemical species at different concentrations (0.1–100 μg mL^{-1}), according to the recommended extraction procedure. Tolerance limit of each species was taken as the largest amount yielding an error in the determination of the analyte not exceeding 5%.

2.6. Recovery and data handling

Recovery evaluations were performed by spiking known amounts of the colours into the samples before processing and comparing the results with those from the same samples prior