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Dispersive solid-phase microextraction and capillary electrophoresis separation of food colorants in beverages using diamino moiety functionalized silica nanoparticles as both extractant and pseudostationary phase

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ABSTRACT

In this work, a new method for the determination of food colorants in beverage samples is developed, using diamino moiety functionalized silica nanoparticles (dASNPs) as both adsorbents in dispersive solid-phase microextraction (dSPME) and pseudostationary phases (PSPs) in capillary electrophoresis (CE) separation. dASNPs were firstly used as adsorbents for the preconcentration of four colorants by the dSPME process. After that, colorants were efficiently separated by CE using 30 mM phosphate buffer (pH 6.0) containing 2 mM β-CD and 0.9 mg/mL dASNPs as additives. All factors influencing dSPME and CE separations were optimized in detail. The investigated analytes showed good linearities with correlation coefficients (R^2) higher than 0.9932. The limits of detection for the four food colorants were between 0.030 and 0.36 mg/L, which are lower than those reported previously. The established method was also used to analyze four colorants in beverage samples with recoveries ranging from 82.7% to 114.6%. To the best of our knowledge, this is the first time to use NPs both as extractants in dSPME and pseudostationary phases in CE for the analytical purpose.

1. Introduction

Food colorants, natural or synthetic, are commonly added to foods to compensate for the loss of natural colors that are destroyed during processing and storage, and to provide the desired colored appearance. However, some synthetic colorants may be pathogenic, especially when they are consumed in excess. At present, about ten kinds of synthetic colorants are permitted to be used as food additives in some countries including China, and their maximum permissible amounts in food are rigidly specified [1] to safeguard consumers' interests. As a result, the analysis of trace colorants in food is of great importance.

Several methods have been widely used to analyze the colorants in food, such as thin-layer chromatography (TLC) [2], gas chromatography (GC) [3], high-performance liquid chromatography (HPLC) [4,5] and HPLC–mass spectrometry (LC–MS) [6]. Among them, HPLC is the most widely used method because it can offer good repeatability and acceptable sensitivity with the traditional UV–vis detection. However, most HPLC methods established for colorant analysis suffer from limited separation ability, and are time consuming especially when the simultaneous determination of a broad range of food colorants is needed. As an alternative method, capillary electrophoresis (CE) has also been used for the analysis of food colorants due to its many advantages, such as high column efficiency, short analysis time and minimal amounts of samples [7–12]. However, lower detection sensitivity, limited selectivity and severe matrix interferences are still drawbacks of the traditional CE technique, which greatly restrain its further use in real sample analysis.

In the past decade, nanoparticles (NPs) have been used in conjunction with CE [13,14], in which they usually worked as pseudostationary phases (PSPs). When NPs are used as PSPs, they are suspended in the electrolytes and are continuously pumped through the capillary by the electro-osmotic flow (EOF) during separation, which guarantees that an entirely fresh dynamic stationary phase is used for every analysis. NPs can also serve as efficient platforms with large surface area for multiple interactions, leading to enhanced separation selectivity and column efficiency. NPs used in CE usually include polymer NPs [15], gold NPs [16], molecularly imprinted polymer NPs [17], latex NPs [18], carbon nanotubes [19] and silica NPs [20–22] etc.

Dispersive solid-phase microextraction (dSPME) [23] is based on the solid-phase extraction (SPE) methodology. In dSPME, the extraction of the analytes is fulfilled by the addition of small

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amount of dispersive solid adsorbents in bulk solution. After extraction, the adsorbents containing the retained analytes are settled by centrifugation or filtration, which are later washed with a small volume of solvent for the desorption of analytes. In the dSPME process, it is much easier for the target analytes to interact fully with the adsorbents, so higher adsorption capacities could be obtained in comparison with those in the traditional SPE. Furthermore, the dSPME method is simple, rapid and cost-effective. Since its emergence, dSPME has received considerable attention and has been recognized as a promising sample pretreatment technique [24–26].

NPs have attracted much attention of the analytical scientists recently due to their higher specific surface area when used as the sorbent materials [27,28]. The introduction of NPs in dSPME will present additional advantages such as quicker mass transfer and shorter equilibrium time [29]. Recently, several kinds of NPs including gold nanoparticles [30,31], carbon nanoparticles [24,32,33], molecular imprinting nanoparticles [34,35] and magnetic nanoparticles [25,29,36] have been used as sorbent materials in dSPME.

In this work, we used dASNPs as sorbent materials in dSPME for the extraction of representative four food colorants: carminic acid, tartrazine, sunset yellow, brilliant blue. The four food colorants are water-soluble dyes with two or three sulfonic groups in their structures (Fig. S1). The pretreated samples were then separated by CE still using dASNPs as PSPs. Under optimized experimental conditions, four food colorants were baseline separated within 8 min. The obtained enrichment factors were 18.6, 18.7, 13.6 and 20.8 for carminic acid, tartrazine, sunset yellow and brilliant blue respectively. The present method was also applied for the determination of colorant additives in some fruit juice beverages with satisfactory results. Some articles concerning the electrophoretic analysis of sulfonated dyes were reported [37,38]. To the best of our knowledge, this is the first report on the use of NPs as both extractants and PSPs for the preconcentration and separation of analytes in real samples.

2. Experimental

2.1. Reagents and materials

All chemicals were analytical grade unless noted otherwise. Double-distilled water (DDW) purified by a Nanopure II system (Barnstead, NH, USA) was used throughout the experiment. Thiourea was purchased from Tianda Kewei (Tianjin, China). Phosphoric acid, sodium hydroxide, sodium dihydrogen phosphate, hydrochloric acid were purchased from Tianjin Guangfu Chemicals (Tianjin, China). Tetraethoxysilane (TEOS) (98%), N-(β-aminoethyl)-γ-aminopropyl triethoxysilane (dATES) were purchased from Guotai-Huarong New Chemical Materials (Zhangjiagang,China). Citric acid, ascorbic acid and benzoic acid were from Heowns Biochemical Technologies (Tianjin, China). β-CD was purchased from Shandong Xinda chemicals (Shandong, China). Malic acid, succinic acid, tartaric acid, tartrazine, sunset yellow, carminic acid and brilliant blue standard solutions were from National information center (Beijing, China).

dASNPs were synthesized according to the method reported previously by our lab [39]. Briefly, a total amount of 1.2 mL of ammonia was added to a conical flask in the presence of 25 mL of EtOH and 2.0 mL TEOS (~9 mmol) by slow stirring. After 24 h of reaction under stirring at 30 °C in thermostatic water bath, the functionalized reagents were added with extra TEOS with the volume ratio of dATES: TEOS=1:1 for particle co-condensation. The amount of functionalized reagents (dATES) added corresponds to approximately 5% (0.45 mmol) of the initial amount of TEOS. The reaction continued for another 24 h, and the particles thus formed were centrifuged and washed with ethanol and DDW repeatedly, then vacuum-dried at 80 °C for 6 h.

dASNPs thus formed are sphere-like, monodisperse and uniform in shape, with an average size of approximately 110 nm. as shown in Fig. 1A.

2.2. Apparatus and operating conditions for CE

TEM tests were carried out on a Philips Tecnai G20 at 200 kV (PHG, Amsterdam, Netherlands). A KH-50B ultrasonic cleaner (Kunshan Hechuang Instrumental, Kunshan, Jiangsu, China) and a QL-901 vortex (Haimen Kylin-Bell Lab Instruments Co., Jiangsu, China) were used to disperse dASNPs in background electrolyte or sample solutions. A TG16-WS centrifuge (Hunan Xiangyi Lab Instruments Co., Changsha, China) was used to centrifuge the samples. The zeta potential of dASNPs was determined with Zetasizer Nano ZS equipments (Malvern Instruments, Worces-tershire, UK). All CE experiments were carried out on a TH-3000 HPCE–HPLC amphibious system equipped with a UV detector and CXTH-3000 data handling software (Tianhui Instruments, Baoding, China). The detection wavelength was set at 220 nm unless noted otherwise. Fused-silica capillaries of 375 μm o.d. and 75 μm i.d. (Yongnian Optic Fiber Co, Hebei, China) were used throughout the experiment.

A capillary with the total length of 36 cm and the effective length of 27 cm was made by scraping off 3–5 mm of the polymer outside the capillary at an appropriate place. Prior to the first use, the capillary was successively rinsed by methanol, DDW, 1 mol/L NaOH, DDW, 1 mol/L HCl, DDW and phosphate buffer solution (PBS) for 20 min each. The EOF was determined by using thiourea as the neutral marker.

Separation voltage was set at 8 kV or −8 kV and current is 40 μA. Electrokinetic injection (−7 kV × 3 s) was selected as the injection mode throughout the experiment. 30 mM PBS (pH 6) with 0.9 mg/mL dASNPs and 2 mM β-CD was employed as background electrolyte solution.

2.3. Preparation of standard solution and food samples

Standard solutions of tartrazine (0.5 mg/mL), sunset yellow (0.5 mg/mL), brilliant blue (0.5 mg/mL) and carminic acid (1.0 mg/mL) were prepared in DDW and stored away from light at 4 °C in refrigerator. The working standard solutions with different concentration were prepared by stepwise diluting the standard solutions with PBS just before use. PBS was prepared by dissolving a certain amount of sodium dihydrogen phosphate in DDW and then adjusted to the appropriate pH value with 1 mol/L NaOH or concentrated

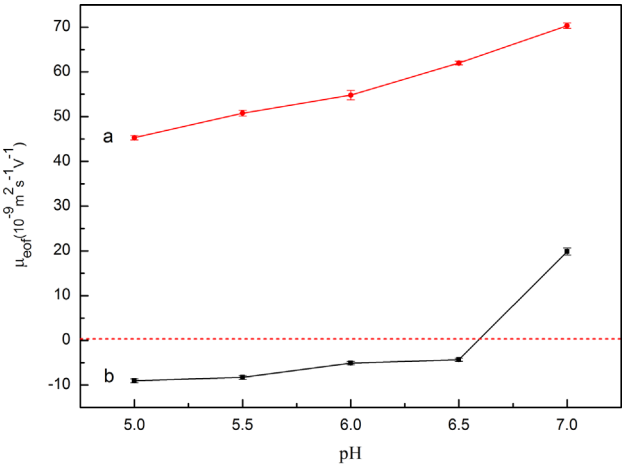

Fig. 1. The effect of buffer solution pH on EOF without dASNPs (a) and with dASNPS (b), (n=3).