



## Short communication

# Fast determination of seven synthetic pigments from wine and soft drinks using magnetic dispersive solid-phase extraction followed by liquid chromatography–tandem mass spectrometry<sup>☆</sup>



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## ABSTRACT

A novel, simple and sensitive method based on the use of magnetic dispersive solid-phase extraction (M-dSPE) procedure combined with ultra-fast liquid chromatography–tandem quadrupole mass spectrometry (UFLC–MS/MS) was developed to determine seven synthetic pigments (tartrazine, amaranth, carmine, sunset yellow, allura red, brilliant blue and erythrosine) in wines and soft drinks. An amino-functionalized low degrees of cross-linking magnetic polymer (NH<sub>2</sub>-LDC-MP) was synthesized via suspension polymerization, and characterized by transmission electron microscopy (TEM). The NH<sub>2</sub>-LDC-MP was used as the M-dSPE sorbent to remove the matrix from the solution, and the main factors affecting the extraction were investigated in detail. The obtained results demonstrated the higher extraction capacity of NH<sub>2</sub>-LDC-MP with recoveries between 84.0 and 116.2%. The limits of quantification (LOQs) for the seven synthetic pigments were between 1.51 and 5.0 µg/L in wines and soft drinks. The developed M-dSPE UFLC–MS/MS method had been successfully applied to the real wines and soft drinks for food-safety risk monitoring in Zhejiang Province, China. The results showed that sunset yellow was in three out of thirty soft drink samples (2.95–42.6 µg/L), and erythrosine in one out of fifteen dry red wine samples (3.22 µg/L), respectively. It was confirmed that the NH<sub>2</sub>-LDC-MP was a kind of highly effective M-dSPE materials for the pigments analyses.

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## 1. Introduction

To protect consumers from health risks, many countries have established strict regulations for the allowable kinds and concentrations of synthetic pigments [1,2]. In China, the common water-soluble synthetic pigments e.g. amaranth, brilliant blue, carmine, sunset yellow, and tartrazine, are permitted in foodstuff [3,4], however, all ingredients including food pigments are required

to be listed on the food labels. Nowadays, more evidence indicates that the abuse of synthetic pigments may cause cancer [2,5], and some people are much sensitive to particular food pigments. Therefore, it is necessary for the determination of synthetic pigments to ensure the food safety.

Today, some high-performance liquid chromatography (HPLC) methods including ultraviolet/visible (UV/vis), diode-array detectors (DAD) [6–10] and mass spectrometry (MS) [2,11,12], have been proposed for the determination of synthetic colorants. In addition, many pretreatment methods, such as liquid–liquid extraction (LLE) and solid-phase extraction (SPE), are used for the extraction of synthetic pigments from various food [2,13], however, these protocols are laborious and time consuming. Luckily, several other cleanup methods based on the traditional SPE technique, such as magnetic solid-phase extraction, dispersive solid-phase extraction (dSPE), micro-solid-phase extraction (µ-SPE) and dispersive

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micro-solid-phase extraction (d- $\mu$ -SPE), have been widely used for multi-residue analyses [14–26]. Although dSPE is considered as one of the most powerful cleanup technologies, to the best of our knowledge, there are no literatures by using dSPE in the analysis of synthetic pigments.

In our previous work, an improved ethylenediamine-functionalized magnetic polymer (IEDA-MP) was found to have an excellent cleanup ability for selective removal of the matrix in red wine [27]. By using IEDA-MP dSPE for cleaning up the studied synthetic pigments, a short sample preparation time and an easy cleanup procedure for the removal of various natural pigments, organic acids and sugars in wine and soft drinks were expected to be achieved, however, some analytes were also adsorbed onto IEDA-MP resulting in low recoveries. The IEDA-MP surface is generally covered with amino groups ( $-\text{NH}-$ ,  $-\text{NH}_2$ ), which provide a special polar hook for enhanced capture of polar analytes. Therefore, we inspired that amino-functionalized low degrees of cross-linking magnetic polymer ( $\text{NH}_2$ -LDC-MP) contained less hydrophilic amino groups and more lipophilic styrene monomer would be probably become a powerful sorbent to carry out magnetic dispersive solid-phase extraction (M-dSPE) for cleaning up the studied synthetic pigments from wine and soft drinks.

In this work, the effect of the usage amount of cross-linker *i.e.*, styrene (St) used in the co-polymerization procedure, which would subsequently lead to obtain various  $\text{NH}_2$ -LDC-MP with different amount of amino groups and lipophilic styrene monomer, on the recovery of seven synthetic pigments has been investigated. In addition, an analytical procedure combined the fast M-dSPE cleanup technique with the LC-MS/MS has been proposed. It has been shown to be effective, fast and accurate in the routine analyses.

## 2. Experimental

### 2.1. Reagents and materials

Ferric chloride, ferrous sulfate, oleic acid (OA), ethanol, methyl methacrylate (MMA), styrene (St), glycidylmethacrylate (GMA), ethylenediamine (EDA), polyvinyl alcohol (PVA 217) and benzoyl peroxide (BPO) of analytical grade were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Primary secondary amine (PSA) was purchased from Agilent Company (Palo Alto, USA). Tartrazine, amaranth, carmine, sunset yellow, allura red, brilliant blue and erythrosine were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Acetonitrile and ammonium acetate (AmAc) of HPLC grade were purchased from Merck Company (Darmstadt, Germany). The wines and soft drinks were acquired on the local markets (Ningbo, China).

### 2.2. Equipment

The characterizations of LDC-MP were carried out by using transmission electron microscopy (TEM) (Hitachi H-7650) (Hitachi, Japan), vibrating sample magnetometer (VSM) (Lake Shore 7410) (Westerville, USA), and elementary analyzer (EA) (ThermoFisher Flash-1112) (ThermoFisher, USA). A vortex mixer Hualida WH-866 (Taicang, China) was used during extraction. UFLC-MS/MS analyses were performed with Prominence UFLC XR system equipped with a LC-20AD pump system, a CTO-20AC column oven, a DGU-20A<sub>3</sub> degasser and a SIL-20AC autosampler (Shimadzu Corporation, Tokyo, Japan) and an AB SCIEX TRIPLE QUAD 5500 mass spectrometer (Applied Biosystems, Foster City, CA, USA). The UFLC-MS/MS system was controlled, and data were analyzed, on a computer

equipped with Analyst 1.5.1 (Applied Biosystems, Foster City, CA, USA).

### 2.3. Synthesis of $\text{NH}_2$ -LDC-MP

The  $\text{NH}_2$ -LDC-MP nanoparticles were prepared by the following steps based on the suspension polymerization and ring-opening reactions. 2.0 g of polyglycol was dissolved into 200 mL of hot water, followed by adding 0.04 mol of MMA, 20 mmol of St and 52 mmol of GMA. Then 2.0 g of OA-M (prepared by the reported procedure [27–30]) was added to the above system under ultrasonication. Finally, 1.0 g of BPO in 20 mL of ethanol was added dropwise under vigorously stirring. The mixture was allowed to react at 80 °C for 3 h, yielding M-co-poly (MMA-St-GMA) polymer. The latter was isolated under magnetic field and washed with water and ethanol to remove redundant MMA, St and GMA.

Exactly 1.25 g of the M-co-poly (MMA-St-GMA) was dispersed into 50 mL of methanol in a 100 mL flask. Then 3.5 mL (50 mmol) of EDA was added dropwise under stirring. The flask was then fitted with a water condenser and heated at 80 °C for 8 h. The final improved amino-functionalized low degrees of cross-linking magnetic polymer named  $\text{NH}_2$ -LDC-MP-I was isolated under magnetic field and washed with water and methanol at pH 7.0 to remove the redundant diamine. Other  $\text{NH}_2$ -LDC-MP nanoparticles, named as  $\text{NH}_2$ -LDC-MP-II,  $\text{NH}_2$ -LDC-MP-III and  $\text{NH}_2$ -LDC-MP-IV, were synthesized in a similar way with different amounts of St (10, 5 and 0 mmol, respectively). All the  $\text{NH}_2$ -LDC-MP nanoparticles were dried in a vacuum oven at 60 °C and stored in a sealed bottle for further use.

### 2.4. M-dSPE procedure

An exactly 1.0 mL of sample was placed into an open evaporating dish and evaporated to dryness in a water bath at 80 °C. Afterwards, the residue was redissolved with pure water (adjusted to pH 9.0 with ammonia 0.5 mol/L) and transferred to a polypropylene centrifuge tube (2.0 mL) containing 15.0 mg of  $\text{NH}_2$ -LDC-MP. The tube was vortexed for 1.0 min, and the adsorbed  $\text{NH}_2$ -LDC-MP was isolated under magnetic field. About 0.5 mL aliquot of the supernatant was filtered using a 0.22  $\mu\text{m}$  membrane prior to its injection into the UFLC-MS/MS system.

### 2.5. LC-QqQ-MS/MS analysis

The chromatographic separation was performed on a Shim-pack XR-ODS II (100 mm  $\times$  2.0 mm i.d., 2.2  $\mu\text{m}$ ) by using 5.0 mmol/L AmAc in acetonitrile as eluent (A), and 5.0 mmol/L AmAc in water as eluent (B) as the mobile phase. The linear gradient was: 0  $\rightarrow$  3.00 min, 2.0  $\rightarrow$  10.0% A; 3.00  $\rightarrow$  7.00 min, 10.0  $\rightarrow$  80.0% A; 7.00  $\rightarrow$  7.01 min, 80.0  $\rightarrow$  2.0% A and 7.01  $\rightarrow$  9.00 min, 2.0% A. The separation was accomplished at a constant flow of 0.40 mL/min. The column was thermostated at 40 °C to increase the retention time reproducibility. The injection volume was 5.0  $\mu\text{L}$ . Mass spectrometry analysis was performed using an electrospray ionization source in negative mode. The operation conditions were as follows: ion spray voltage,  $-4500$  V; curtain gas (CUR), 40 psi and interface heater was on; collision gas, medium; nebulizer gas (gas 1) and heater gas (gas 2), 50 and 50 psi; the turbo spray temperature, 500 °C; entrance potential (EP),  $-10$  V; collision cell exit potential (CXP),  $-10$  V. Nitrogen was used in all cases. Multiple-reaction monitoring (MRM) mode was used for quantification. The results of the precursor ion, product ion are shown in Table 1. Applied Biosystems/MDS Sciex Analyst software (versions 1.5.1) was used for data acquisition and processing.

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