



Analytical Methods

Conducting polymer modified screen-printed carbon electrode coupled with magnetic solid phase microextraction for determination of caffeine



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ABSTRACT

In the current study, we introduce magnetic solid phase microextraction coupled with electrochemical detection of caffeine. A commercially available disposable screen-printed carbon electrodes modified with poly Alizarin Red S are employed as electrochemical sensors in the detection stage. However, the suitability of magnetic solid phase microextraction for electroanalytical methods such as square wave voltammetry has not been declared. With our optimised conditions in hand, the system response was linearly proportional to the concentration of caffeine in the range of 0.5–20 μM with a correlation coefficient of about 0.9987. The detection limit of the sensing system was found to be 0.05 μM (a signal-to-noise ratio of 3). At the end of the study, the suitability of this new procedure for the analysis of energy drink, soft drink, and chocolate milk samples was demonstrated.

1. Introduction

Caffeine (CAF) is a natural stimulant, most commonly found in some plant species such as tea, coffee and cacao plants. Caffeine is present naturally or added to widely consumed foods. It is also found in cola-type soft drinks and energy drinks that mainly contain artificial CAF. However, too much CAF consumption can cause the muscles effects of a move erratically. The quantity of the CAF in the matrix, whether it is the major compound or if it is found in trace quantity, is the very important topic.

Generally, direct determination of target species (organic or inorganic species) in complex matrices is difficult due to their usually low-level concentrations and matrix interferences. Low-level detection of target species in various kinds of samples generally requires a pre-treatment process to isolate and preconcentrate them before instrumental measurements. Conventionally, various extraction procedures have been declared for isolation and preconcentration of low-levels of CAF such as accelerated solvent extraction (ASE) (Bermejo et al., 2013; Ding, Zhang, Gu, Xagorarakis, & Li, 2011), liquid–liquid extraction (LLE) (McCusker, Goldberger, & Cone, 2006), and solid-phase extraction (SPE) (Farrington, Magner, & Regan, 2006; Rodrigues et al., 2007; Theodoridis & Manesotis, 2002; Tian, Yan, & Row, 2010). LLE and SPE are dominant techniques for sample preparation. Among these, SPE approach has well-known operating disadvantages (e.g. requires large amounts of organic solvents, time-consuming, and labor-intensive). SPE is one of the most widely employed techniques for the isolation and preconcentration of CAF (Theodoridis & Manesotis, 2002; Farrington et al.,

2006; Rodrigues et al., 2007; Tian et al., 2010). However, the SPE methodology suffers from some inconveniences depending upon the kind of SPE applied, the sample characteristics, and the sorbent employed.

Microextraction methodology saves sample preparation time and can improve sensitivity and selectivity of target analytes (Herrero-Latorre, Barciela-García, García-Martín, Pena-Creciente, & Otarola-Jimenez, 2015; Souza-Silva, Risticvic, & Pawliszyn, 2013). In recent years, several types of research have been devoted to the development of new microextraction concepts of sample preparation. Actually, different types of microextraction techniques were reported such as; hollow fibre liquid phase microextraction (HF-LPME) (Xiong, Chen, He, & Hu, 2010), single-drop liquid microextraction (SDLME) (Timofeeva, Medinskaia, Nikolaeva, Kirsanov, & Bulatov, 2016), dispersive liquid-liquid microextraction (DLLME) (Sereshti & Samadi, 2014), in-syringe dispersive liquid-liquid microextraction (IS-DLLME) (Frizzarin, Maya, Estela, & Cerdà, 2016), headspace solid-phase microextraction (HS-SPME) (Müller, Vetter, Richter, & Bracher, 2014), and solid phase microextraction (SPME) (Pawliszyn, Yang, & Orton, 1997). Most of these microextraction procedures have been routinely used in combination with gas and liquid chromatography. However, these methods require delicate and costly instruments which require trained staff to employ. In addition, SPE coupled to electrochemical detection on glassy carbon electrode has been developed for the determination of CAF in acetonitrile (Chan & Webster, 2016).

Magnetic solid-phase extraction (m-SPME) is a new approach for the enrichment of target analytes from large volumes based on the use of magnetic or magnetizable adsorbents. In this regard, the replacement of CNTs to obtain magnetic-CNTs (m-CNTs) have been researched in the

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last decade to transform CNTs into convenient sorbents for use in m-SPME (Herrero-Latorre et al., 2015; Xie, Jiang, Zhu, Liu, & Ouyang, 2014). Magnetic isolation and enrichment using m-CNTs ensured the effective sample pre-treatment operations. In an m-SPME system, the m-CNT adsorbents are transferred to the analysis solution and the target species are quickly adsorbed onto the surface of the m-CNTs (Herrero-Latorre et al., 2015; Masotti & Caporali, 2013). After extraction is complete, the analyte loaded magnetic carbon nanotubes are isolated from the aqueous solution by applying an external magnetic field and, the analyte is collected from the magnetic sorbent by elution with a suitable solvent. Afterwards, the concentrations of analyte in the microvolume of the samples were determined by distinct analytical techniques (Deng et al., 2005; Jin et al., 2007; Karousis, Tagmatarchis, & Tasis, 2010; Korneva et al., 2005; Qu, Huang, Yu, Chen, & Kong, 2008; Stoffelbach, Aqil, Jérôme, Jérôme, & Detrembleur, 2005). Nevertheless, the suitability of m-SPME for electroanalytical methods, such as square wave voltammetry, has not been announced. Electrochemical devices offer unique attributes to address the challenges of analytical chemistry. The primary advantages of electrochemical devices include the possibility of miniaturization and portability. Previously, several modified electrodes (GCE or CPE) were reported for the determination of CAF. For these purposes, a great variety of electrode materials have been tried, such as conducting polymers, molecularly imprinted polymers, Nafion, metal nanoparticles, carbon nanotubes (CNTs), and graphene (GR) (Jin et al., 2007; Kan et al., 2012; Khoo, Pumera, & Bonanni, 2013; Korneva et al., 2005). Spite of the development of various types of carbon electrodes for the determination of CAF, preparation of these electrodes can be tedious and time-consuming (*i.e.* the polishing processes) and the modified electrodes may not be entirely reproducible between measurements, especially if the preparation method does not lead to electrodes with identical surface areas (Chan & Webster, 2016). On the other hand, the major drawback of CPEs, which limits their applicability in the practical assay, is that electrochemical assay with carbon paste-based electrodes requires an adequate experience of the user (Sanghavi, Wolfbeis, Hirsch, & Swami, 2015). A use of disposable screen-printed carbon electrodes (SPCEs) can be eliminated these aforesaid drawbacks (*i.e.* the polishing processes, the limits of the applicability, and the user experience). Disposable SPCEs are portable, economical, and disposable devices, which are ideal and suitable for working with micro-volume samples as small as 50 μL . Besides, the disposable SPCEs surface can be easily modified with the mediators, conducting polymers or nanostructures for their use in chemical and biosensors as a transducer to enhance the electron transfer rate (Mettters, Kadara, & Banks, 2011).

In this work, we introduce magnetic solid phase microextraction coupled with electrochemical detection. Screen-printed carbon electrode-based electrochemical detection has been successfully combined with m-SPME for the first time. SPCEs modified with conducting polymer (poly-alizarin red S; poly(ARS)) are employed as electrochemical transducers in the analyte detection stage. m-SPME is a well-known process for the enrichment of hydrophobic species from water sample without the use of toxic organic solvents. Nowadays, miniaturization of both analytical instrumentation and analytical methodologies has become very popular, and many efforts have focused on carrying out chemical analysis at a reduced scale (Crew, Cowell, & Hart, 2008; Fernández et al., 2014, 2015).

2. Experimental

2.1. Apparatus

The morphology of the poly(ARS) modified SPCE was characterized by using scanning electron microscopy (SEM, FEI Quanta 450 FEG-EDS Field Emission Scanning Electron microscope). Square wave voltammetry (SWV) evaluations were done using a Gamry Reference 600

potentiostat (Gamry, USA). For electrochemical measurements, commercial SPCE (DRP-110; dimensions L33 \times W10 \times H 0.5 mm) was obtained from DropSens and consisting of a carbon working electrode, a carbon counter electrode, and a silver pseudo-reference electrode printed on a substrate. The disposable SPCE has an electrochemical cell of 50 μL . A boxed connector (DRP-BICAC connector); dimensions 8.0 \times 4.0 \times 3.5 cm) operated as an interface between a commercial SPCE and Gamry Reference 600 potentiostat.

2.2. Reagents

All chemicals were of analytical reagent purity used as provided. Distilled water was used for solution preparation and dilution. Caffeine and Alizarin red S was purchased from Sigma–Aldrich (Austria) and used without any further refinement. The stock solution of CAF (1.0×10^{-3} M) was prepared by dissolving of the appropriate quantity of CAF in 100 mL of distilled water and stored at 4 $^{\circ}\text{C}$ in the dark. The lowest concentrations were freshly prepared on the day of the experiment by appropriate dilution of the stock with acetate buffer. The phosphate buffer solutions (PBS) were prepared and used subsequent studies. 0.1 M acetate buffer solution (pH 4) was employed as the supporting electrolyte for electrochemical determination CAF. Carrez I solution and Carrez II solution (Carrez, 1908) were prepared by dissolving 21.9 g of $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in 100 mL of distilled water and 10.6 g of $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in 100 mL of distilled water, respectively.

2.3. Sample preparation

Commercially samples (*i.e.* energy drink, soft drink, and chocolate milk) were purchased from local supermarkets and analysed. All measurements were performed in triplicate. Once sample bottles were open, the drinks were degassed, homogenized and filtered. Filtered drink samples were diluted with phosphate buffer (pH 7) water to make 1.0×10^{-6} CAF solutions.

The chocolate milk samples might contain proteins, fats, and carbohydrates that interfere with the analysis. Carrez clarification reagents (Carrez, 1908) remove these interfering compounds from the analytes. This method has previously been used and validated with coffee and potatoes matrix (Culhaoglu, Zheng, Méchin, & Baumberger, 2011). In this context, A 5 mL chocolate milk sample was pipetted into 10 mL polypropylene centrifuge tubes. After that, 1.0 mL of Carrez I reagent was added and afterwards 1.0 mL of Carrez II and the pH was adjusted to 7.5–8.0 by addition of 1.0 M NaOH. After pH adjustment, the final solution centrifuged at 5000 rpm for 5 min. The supernatant was filtered using a 0.45 mm filter and the volume was adjusted to 50 mL with phosphate buffer solution (pH = 7.0). A 10 mL aliquot of this solution was extracted and analysed.

2.4. Preparation of Fe_3O_4 -MWCNTs sorbent

The magnetic nanoparticles were synthesised according to a previously published description (Fan & Li, 2012; Huang, Deng, & Zhang, 2014; Moliner-Martínez, Prima-García, Ribera, Coronado, & Campíns-Falcó, 2012; Pistone et al., 2014; Sowichai et al., 2012;). Classically, Fe (III) and Fe(II) salts (2:1 M ratio) were dissolved in concentrated HCl (~ 1.0 mL) and the solution volume was made up to 10 mL with distilled water. Then, 0.5 g of MWCNTs was dispersed in 20 mL of distilled water and the solutions were carefully combined under a nitrogen atmosphere. Then, 50 mL of 3 M NH_4OH solution was added dropwise to precipitate the iron oxides (at 50 $^{\circ}\text{C}$) under inert conditions to prevent the oxidation of Fe (II). The MWCNTs– Fe_3O_4 NPs were separated using a powerful magnet and washed repeatedly with distilled water until pH 7.0. After that, the MWCNTs– Fe_3O_4 NPs were rinsed with ethanol and dried at 50 $^{\circ}\text{C}$ for 2 h.

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