Magnetic solid phase microextraction for determination of caffeine coupled with poly (Alizarin Red) modified screen-printed carbon electrode detection

Hayati Filik, Asiye A. Avan
Istanbul University, Faculty of Engineering, Department of Chemistry, Istanbul, Turkey

Abstract

In the current study, we introduce magnetic solid phase microextraction (m-SPME) coupled with electrochemical detection of caffeine. A commercially available disposable screen-printed carbon electrodes modified with poly Alizarin Red S (poly(ARS)) are employed as electrochemical sensors in the detection stage. However, the suitability of m-SPME for electroanalytical methods such as square wave voltammetry (SWV) has not been declared. With our optimized 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 (LOD) of the sensing system at a signal to noise ratio of 3 was 0.05 μM. At the end of the study, the suitability of this new procedure for the analysis of energy drink and soft drink samples was demonstrated.

Introduction

Caffeine (CAF) is a natural stimulant most commonly found in some plant species. 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 for 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. We introduce magnetic solid phase microextraction coupled with electrochemical detection. 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(ARS) are employed as electrochemical transducers in the analyte detection stage.

Methods and Materials

10 mg of Fe_3O_4 coated MWCNTs was added into a test tube. Then, dispersed Fe_3O_4 coated MWCNTs solution was transferred quickly into 10 mL sample solution (containing 1.0 μM CAF) . After adjusting the pH to 7.0 with 0.1 M phosphate buffer, the mixture was vortexed for 2 min. Thereafter, the Fe_3O_4 coated MWCNTs were separated from the supernatant solution by a magnetic field and the upper water phase was decanted. 500 μL of elution solvent (*i.e.* ethanol) was added to CAF/Fe_3O_4/MWCNTs and the mixture was minutely vortexed for 5 min. After desorption is completed, the organic phase (*i.e.* ethanol phase) was separated and the eluate was evaporated at ambient temperature (or at 50ºC) until dry and re-dissolved in 200 μL acetate buffer (pH 4). The final solution (50 μL) was transferred directly into the working electrode area and the oxidation peak current of CAF was recorded with SWV.

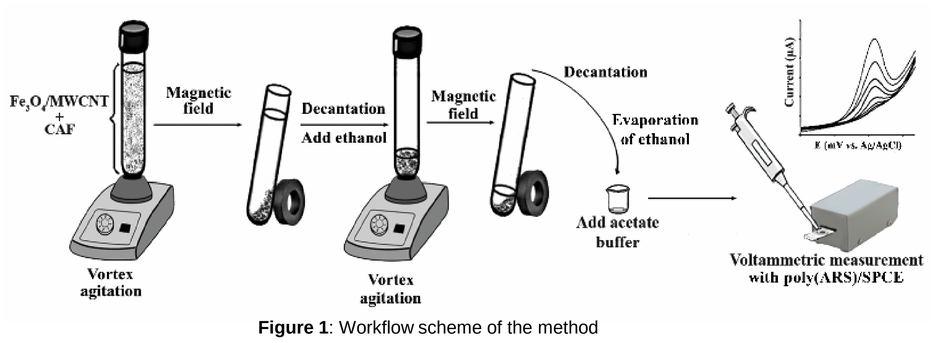


Figure 1: Workflow scheme of the method

The poly(ARS) was synthesized according to previously published methods. Poly (ARS) deposited on the commercial SPCEs by the electrochemical polymerization of ARS (0.1 mM) present in 0.1 M PBS (pH 7). The SPCE was attached to the boxed connector for the electrochemical polymerization process. Then, an aliquot of 50 μL of PBS containing 0.1 mM ARS solution was dropped on the commercial SPCE surface. After that, chronoamperometry was used to deposit poly (ARS) films on SPCE surface using a constant potential at 1.4 V for 30 s.

Results

In order to reach equilibrium status, the most important ground factors affecting the adsorption and desorption operation such as pH, time of extraction, the quantity of sorbent, the volume of the suitable elution solvent, and elution time were tested to reach the best extraction efficiency. The recovery percentage of CAF was calculated as follows:

$$\text{Recovery}(\%) = \frac{C_{or} V_{es}}{C_{aq} V_{aq}} \times 100$$

where C_{or}, C_{aq}, V_{es} and V_{aq} are the CAF concentration in the ethanol phase, the original concentration of CAF in the aqueous phase, the volume of elution solvent, and volume of the aqueous phase, respectively.

Effect of pH- sorbent amount- elution time

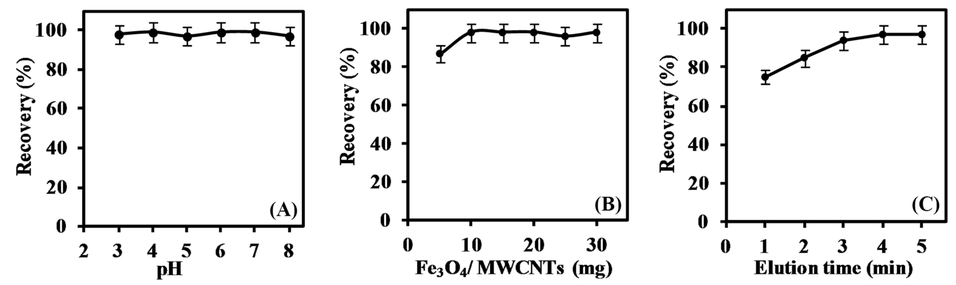


Fig. 1. (A) Effect of elution time on the extraction recovery of CAF. 0.1 M phosphate buffer (pH 7), 2 min adsorption time, 5 min desorption time, 10 mg Fe_3O_4/ MWCNTs. (B) Effect of sorbent amount on the extraction recovery of CAF. Extraction conditions: 0.1 M phosphate buffer (pH 7), 2 min adsorption time, 5 min desorption time. (C) Effect of pH on the recovery of CAF. 0.1 M acetate buffer (pH 4), 0.1 mM CAF, scan rate 50 mV s^{-1}.

Analytical Performance

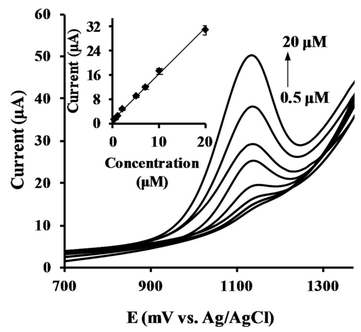


Figure 2. Experimental conditions and inset: Acetate buffer (pH 4), C_{CAF}=0.5 ,0.8, 1.0, 2.0, 5.0, 7.0, 10, and 20 μM. SWV parameters: Step size 8 mV, frequency 10 Hz, pulse size 100 mV. Extraction conditions: pH 7, 10 mg Fe_3O_4/ MWCNTs sorbent, 2 min adsorption time, 5 min desorption time.

Method validation such as linearity, correlation coefficients, and LODs was investigated. The standard curve was performed in triplicate after m-SPME. The standard curve of CAF is reached in the concentration range of 0.5–20 μM.

I = 1.5137 C + 1.3593 (R^2 = 0.9974, n = 3) LOD= 0.05 μM (S/N=3). The reproducibility of the coupled method was tested from five consecutive determinations for 1.0 μM CAF and the relative standard deviation (RSD %) obtained was 4.4 % which shows good enough reproducibility of the determinations (*i.e.* after extraction) at the modified electrode. This coupled method demonstrated that the conducting polymer modified SPCE (poly(ARS)/SPCE) can be a very promising voltammetric sensor for the trace analysis of CAF after m-SPME.

Real Sample Analysis

Table 1. Analytical results of real samples by m-SPME/SWV

Sample	Declared (mg/L)	UV-vis	Standard added (mg/L)	Found (mg/L)	Recovery (%)
Energy drink	150	149.5±3	-	148.69±1.0	-
			20	168.87±0.9	101
			40	188.95±1.1	101
Soft drink (cola)	80	79.5±4	-	79.61±1.92	-
			20	99.85±2.3	101
			40	120.68±1.88	103

Conclusions

CAF was enriched with Fe_3O_4 coated MWCNTs sorbent, and a poly (ARS)/SPCE-SWV method was established for the analysis of trace CAF in drink samples. The present poly (ARS)/SPCE is suitable for accurate and precise determination of trace amounts of CAF molecules in complex matrixes. Screen-printed carbon electrode-based voltammetric quantification has been successfully combined with m-SPME for the first time. The analytical method integrated miniaturised systems both in sample preparation and in detection stage, with the major benefit of avoiding costly and bulky or unmovable instrumentation. This method reflects that the superior sensing activity of the proposed sensor is highly reproducible, which also dooms the applicability of the sensor. The suggested combined method has the following benefits such as simple, rapid, and low analysis time and low cost.

Contact

Hayati Filik
Istanbul University, Faculty of Engineering, Department of Chemistry, 34320 Avcılar Istanbul, Turkey
E mail: filik@istanbul.edu.tr
Phone: +90 212 473 70 70/17739

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