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Microwave-Assisted Density-Tunable Dispersive Solid-phase Microextraction for the Determination of Tetracycline in Urine Samples Prior to HPLC-DAD Analysis

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Abstract

Background: The development of rapid, sensitive, and environmentally friendly sample preparation methods is important for monitoring antibiotic residues in complex biological matrices. **Objective**: The objective of this study was to develop a novel microwave-assisted density-tunable dispersive solid-phase extraction (MA-DT-DSPE) method for the extraction and preconcentration of tetracycline from human urine samples prior to high-performance liquid chromatography with diode array detection (HPLC-DAD). **Materials and Methods**: The proposed method employed a low-density organic sorbent (safranal) dissolved in a volatile dispersive solvent and rapidly injected into the aqueous sample. Microwave irradiation caused instantaneous volatilization of the dispersive solvent, resulting in in-situ formation and homogeneous dispersion of fine sorbent droplets without mechanical agitation. Because the sorbent was less dense than water, the analyte-enriched phase floated to the surface for easy collection. The effects of dispersive solvent type and volume, sorbent mass, microwave power, irradiation time, and ionic strength were systematically optimized. **Results**: Under optimal conditions, the method showed a low limit of detection of 0.26 ng mL^{-1}, linearity over 0.8–200 ng mL^{-1} ($R^2 \geq 0.994$), extraction recovery of 74%, and precision better than 5.6% relative standard deviation. Analysis of spiked urine samples gave relative recoveries of 96%–107%, indicating negligible matrix effects. **Conclusions**: It can be concluded that the MA-DT-DSPE-HPLC-DAD method is a rapid, simple, sensitive, reproducible, and eco-friendly analytical approach, making it a promising alternative for the routine determination of tetracycline residues in human urine samples.

Keywords: Dispersive solid phase extraction; high-performance liquid chromatography; Mass spectrometry; Tetracycline; Safranal; Urine samples

Introduction

Global demographic trends, including population growth, urbanization, and shifting consumption behaviors, have significantly increased the reliance on pharmaceutical agents in recent decades. These compounds, while essential for disease prevention, diagnosis, and treatment, are now recognized as emerging contaminants due to their widespread and sometimes excessive use. The resultant accumulation of pharmaceutical residues in biological samples has become a subject of increasing analytical and toxicological concern, prompting the development of sensitive monitoring strategies [1-4]. Tetracycline, a broad-spectrum antibiotic, is characterized by high biological activity and notable chemical stability, which collectively underpin its persistence in biological systems. Its pharmacokinetic profile predisposes the compound to accumulation at non-therapeutic concentrations in biological fluids, often resulting from improper dosing, overuse, or bioaccumulation [5, 6]. Such deviations can compromise therapeutic efficacy, induce toxicity, and contribute to the emergence of antimicrobial resistance. Accordingly, the accurate and reliable determination of tetracycline residues in biological matrices is essential for public health surveillance and comprehensive risk assessment [7, 8]. Sophisticated analytical techniques, particularly gas and liquid chromatography (GC and LC) interfaced with sensitive detection systems such as mass spectrometry (MS), are powerful tools for pharmaceutical analysis [9, 10]. However, direct application to real samples is often hindered by matrix complexity, interfering substances, and trace analyte concentrations, which can compromise analytical figures of merit. Hence, an efficient sample preparation and preconcentration step is indispensable prior to instrumental determination [11, 12]. While conventional methods such as solid-phase extraction (SPE) and liquid-liquid extraction (LLE) are commonly employed, modern microextraction techniques have emerged as superior alternatives. These approaches reduce labor, processing time, and solvent consumption while enabling significant analyte enrichment, high recoveries, and faster analysis. Among these, dispersive solid-phase extraction (DSPE) represents a notable advancement, effectively supplanting traditional SPE protocols [13, 14].

While conventional solid-phase extraction has been widely adopted for sample preparation, the innovative dispersive solid-phase extraction overcomes many limitations of its predecessor. Traditional SPE entails labor-intensive, multi-step protocols involving column conditioning and equilibration, leading to prolonged analysis times. By contrast, DSPE simplifies the workflow through direct dispersion of solid sorbents into the sample matrix, eliminating preparatory steps and enhancing efficiency. The sorbent portfolio for DSPE has diversified considerably, encompassing silica-based materials (e.g., octadecylsilane [15]), carbonaceous nanostructures (graphene oxide [16], multi-walled carbon nanotubes [17]), molecularly imprinted polymers [18], and crystalline porous frameworks—specifically metal-organic frameworks and covalent organic frameworks—comprising metallic nodes interconnected by organic linkers [19–21]. These adsorptive materials provide exceptional target specificity, facilitating efficient isolation and preconcentration of analytes from complex biological and environmental matrices.

This study presents a modified density-tunable dispersive solid-phase extraction (DT-DSPE) method for tetracycline determination in urine by HPLC-DAD. Safranal was employed as the sorbent, dispersed without mechanical agitation by dissolving it in a volatile solvent and inducing vaporization via microwave irradiation. This process released fine sorbent particles uniformly throughout the solution; owing to safranal's low density, the analyte-enriched phase floated to the surface for easy collection. Microwave irradiation simultaneously accelerated solvent evaporation and enhanced analyte migration onto the sorbent. This approach yields substantially preconcentrated, purified extracts suitable for sensitive instrumental analysis.

Materials and Methods

Chemicals and Reagents

Analytical standards of tetracycline were obtained from Dr. Ehrenstorfer (Augsburg,

Germany). Analytical-reagent grade safranal, methanol, acetonitrile, formic acid, NaCl, chloroform, and dichloromethane were purchased from Merck (Darmstadt, Germany). Also, HPLC–grade water was bought from Merck (Darmstadt, Germany). A stock of tetracycline, at 1000 mg L-1, was prepared in methanol. Diluted analyte solutions were prepared immediately prior to use by precise volumetric dilution of the stock solution with ultra-pure water.

Instrumental Setup

Quantitative analysis of tetracycline was conducted using an Agilent 1200 liquid chromatograph (Agilent Technologies, USA) coupled with a diode-array detector. Chromatographic separation was accomplished on a Gemini C18 column (150 mm × 4.6 mm, 5 µm particle size) obtained from Phenomenex (Torrance, CA, USA). The column temperature was maintained at 30°C to ensure consistent retention behavior and optimal peak symmetry. The mobile phase consisted of acetonitrile (solvent A) and water containing 1% formic acid (solvent B) mixed in an isocratic ratio of 70:30 (v/v), delivered at a constant flow rate of 0.7 mL min^{-1}. Detection was performed at 350 nm, the wavelength at which tetracycline exhibits maximum UV-Vis absorption. Sample injections were performed manually using a fixed 20 µL injection loop, ensuring reproducible injection volumes and minimizing variability between samples.

Real Samples

Urine samples were collected from healthy volunteers in Baghdad, Iraq. Upon collection, all specimens were immediately frozen and maintained at −20 °C until further processing. Before the extraction step, the samples were thawed and brought to room temperature to ensure consistency during the subsequent preconcentration procedure.

Procedure

A 5 mL urine aliquot containing tetracycline was transferred to a glass test tube, and NaCl was added to achieve 1% (w/v) concentration. Safranal (20 mg) was dissolved in 0.3 mL chloroform and carefully placed at the tube bottom. The tube was subjected to microwave irradiation (180 W, 25 s), inducing rapid chloroform volatilization and uniform dispersion of safranal particles throughout the solution. These dispersed particles adsorbed the analyte and, due to safranal's lower density, floated to form a surface layer. After complete solvent evaporation, the enriched sorbent was collected with a spatula, re-dissolved in 20 µL mobile phase, and injected into the HPLC-DAD system for analysis.

Results and Discussion

Optimization of Effective Parameters

Dispersive Solvent Type

The efficiency of the DT-DSPE procedure is contingent upon the selection of a suitable disperser solvent for safranal, which must exhibit adequate solvating capacity, high vapor pressure, and a density greater than water to ensure localization at the bottom of the reaction vessel. To identify the most effective solvent, three candidates-chloroform, dichloromethane, and dichloroethane-were evaluated under identical experimental conditions. As depicted in Fig. 1a, chloroform yielded the highest extraction recovery for tetracycline, outperforming both dichloromethane and dichloroethane. This superior performance is likely attributable to the more uniform dispersion of safranal particles achieved with chloroform. By contrast, the partial miscibility of dichloromethane and dichloroethane with the aqueous phase may have increased the solubility of tetracycline in the sample solution, thereby diminishing its availability for sorption onto safranal [22, 23]. On the basis of these results, chloroform was selected as the optimal disperser solvent and employed throughout the remainder of this study.

Optimization of Chloroform Volume

Optimization of the disperser solvent volume was subsequently investigated as a key parameter affecting method performance. Chloroform volumes ranging from 0.2 to 0.7 mL were evaluated (Fig. 1b). Extraction efficiency increased with volume up to 0.3 mL, reflecting enhanced sorbent dispersion and increased contact area. Beyond 0.3 mL, recoveries declined due to increased analyte solubility in the aqueous phase, reducing sorption onto safranal [23]. Incomplete

dispersion at 0.2 mL also yielded suboptimal recovery. Thus, 0.3 mL chloroform was selected as optimal.

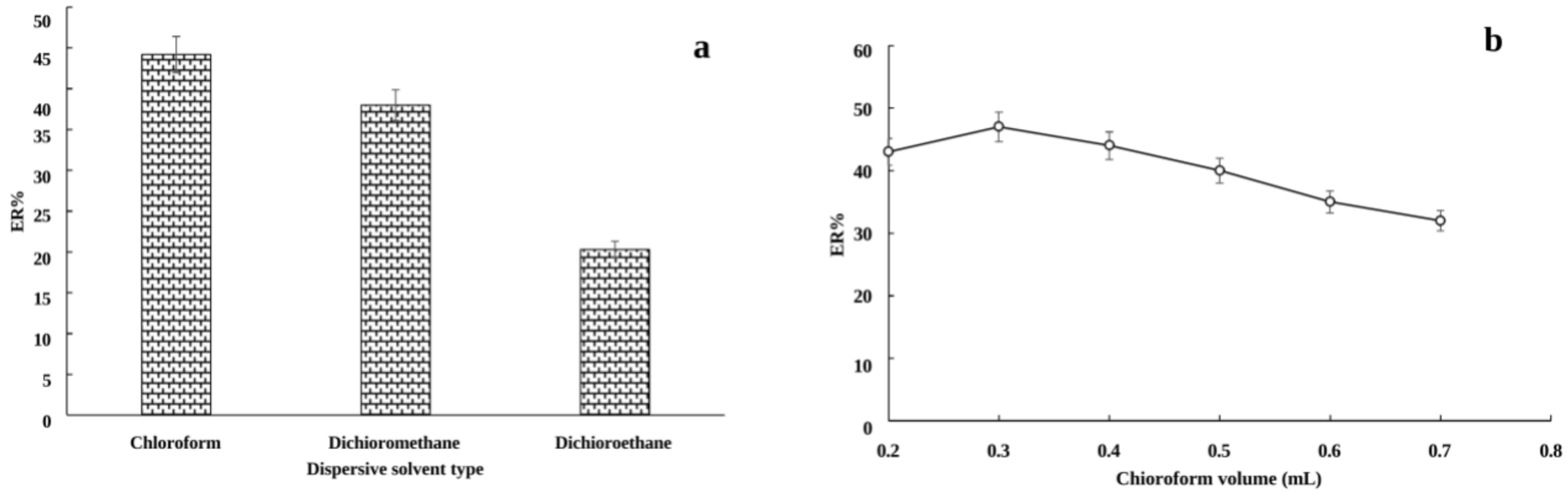

Figure 1. Optimization of dispersive solvent type (a) and chloroform volume (b).

Extraction conditions in Figure 1b were the same as those in Figure 1a, except that chloroform was used as the dispersive solvent.

Safranal Amount

The sorbent quantity is a critical parameter affecting extraction efficiency in DT-DSPE. Safranal masses ranging from 5 to 40 mg were evaluated using solutions of identical analyte concentration (Fig. 2a). Extraction recovery (ER) increased with sorbent mass up to 20 mg, reflecting greater availability of adsorption sites. Beyond 20 mg, recoveries declined due to incomplete analyte elution and poor sorbent dispersion [23]. Insufficient sorbent (<20 mg) provided inadequate adsorption sites, reducing extraction efficiency. On the basis of these findings, a safranal mass of 20 mg was established as the optimal condition and adopted for all subsequent experiments.

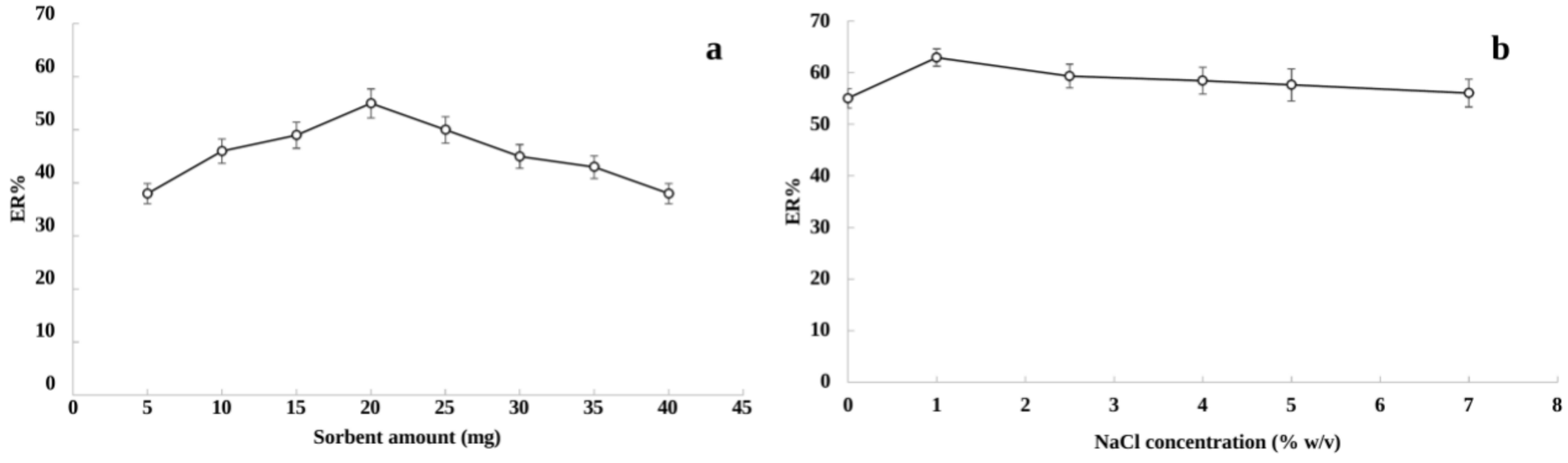

Figure 2. Selection of safranal amount (a) and study of ionic strength (b).

Extraction conditions in Figure 2a were the same as those in Figure 1b, except that 0.3 mL of chloroform was selected as the dispersive solvent volume. Extraction conditions in Figure 2b were the same as those in Figure 2a, except that 20 mg safranal was used as the sorbent.

Ionic Strength

From a theoretical standpoint, the presence of salt in an aqueous solution can exert dual and opposing effects on extraction efficiency. The salting-out effect enhances analyte recovery by decreasing its solubility in the aqueous phase through ionic strength-induced modifications to solution polarity. Conversely, the salting-in effect reduces extraction efficiency by increasing solution viscosity, which lowers analyte diffusion coefficients and impedes mass transfer to the sorbent [24]. In the present work, the influence of NaCl concentration on the extraction performance of the DT-DSPE method was systematically evaluated over the range of 0–7% (w/v), with the corresponding results depicted in Fig. 2b. Extraction recoveries increased progressively with NaCl concentration up to 1% (w/v), reflecting the dominance of the salting-out effect, which enhanced analyte partitioning toward the safranal sorbent. At NaCl concentrations exceeding 1% (w/v), recoveries reached a plateau and remained relatively constant. This behavior suggests that beyond the optimal ionic

strength, the incremental benefits of the salting-out effect are counterbalanced by the onset of the salting-in effect, manifested as increased solution viscosity and reduced analyte diffusivity. Consequently, a NaCl concentration of 1% (w/v) was established as the optimal condition and employed in all subsequent experiments.

Microwave Exposure Time and Power

Microwave irradiation was employed in this methodology to facilitate the extraction procedure and enhance its analytical performance. The applied microwave energy serves two primary functions: it elevates the sample temperature, inducing rapid vaporization of the chloroform disperser, and simultaneously reduces the viscosity of the aqueous medium, thereby increasing analyte diffusion rates and improving mass transfer toward the sorbent [25]. Systematic optimization of microwave parameters was undertaken by evaluating the effects of irradiation time and power on ER, with the results depicted in Fig. 3. As shown in Fig. 3a, extraction efficiency increased markedly as irradiation time was extended from 5 to 25 seconds, reflecting progressive solvent evaporation and enhanced analyte-sorbent interaction. Beyond 25 seconds, recoveries plateaued, indicating that complete chloroform removal and optimal extraction had been achieved within this period. The influence of microwave power was similarly assessed across 90, 180, and 360 W (Fig. 3b). Optimal extraction performance was observed at 180 W, which provided sufficient energy for efficient solvent vaporization and analyte migration. At 90 W, incomplete chloroform evaporation limited extraction efficiency, while at 360 W, excessive thermal input may have compromised analyte stability or sorbent integrity, leading to reduced recoveries. Based on these observations, microwave irradiation at 180 W for 25 seconds was established as the optimal condition for subsequent experiments.

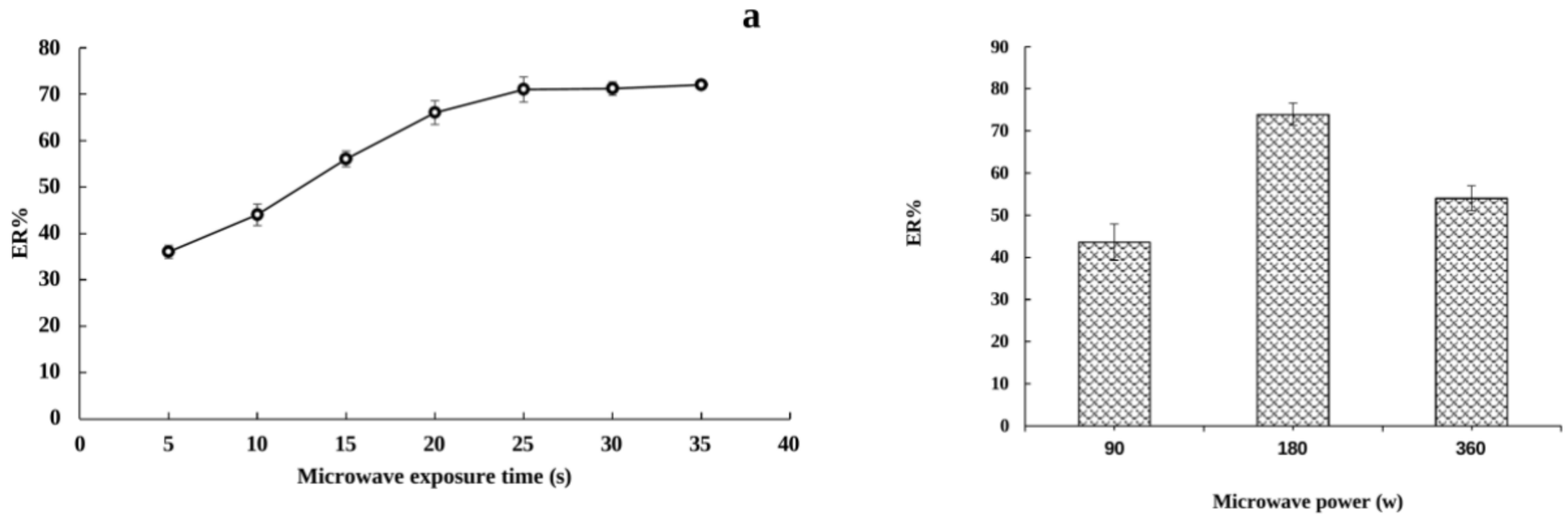

Figure 3. Optimization of microwave exposure time (a) and microwave power (b).

Extraction conditions in Figure 3a were the same as those in Figure 2b, except that 1% (w/v) NaCl was added to the sample solution. Extraction conditions In Figure 3b, the same as those in Figure 3a, except that 25 s was selected as the microwave exposure time.

Analytical Method Validation

The analytical performance of the developed DT-DSPE-HPLC-DAD method was validated in accordance with SANTE guidelines (European Commission). Key validation parameters, including limit of detection (LOD), limit of quantification (LOQ), linearity (LR), precision (relative standard deviation (RSD)), and ER, were systematically evaluated. Calibration studies were performed by preparing standard solutions spanning the concentration range of 0.8–200 ng mL^{-1}, with each concentration analyzed in triplicate. The method exhibited excellent linearity, as evidenced by determination coefficients (r^2) consistently exceeding 0.994. The LOD, calculated at a signal-to-noise ratio of 3, was 0.26 ng mL^{-1}, while the LOQ (signal-to-noise ratio of 10) was established at 0.8 ng mL^{-1} in

deionized water. Precision was assessed through intra-day and inter-day repeatability studies, with RSD values below 5.6%, confirming acceptable method reproducibility. The enrichment factor, representing the extent of analyte preconcentration, was calculated as the ratio of analyte concentration in the final organic phase (Corg) to that in the initial aqueous sample (Caq).

$EF = C_{org}/C_{aq}$

The ER percentage, which reflects the efficiency of the extraction process, was calculated using the following formula:

$ER(\%) = (C_{org} \times V_{org})/(C_{aq} \times V_{aq}) \times 100$

where V_{org} and V_{aq} represent the volumes of the final organic phase and initial aqueous sample, respectively.

Analysis of genuine urine samples using the developed method resulted in an extraction recovery of 74%, indicating satisfactory efficiency for the determination of tetracycline in real biological specimens. All validation data are comprehensively presented in Table 1.

Table 1. Analytical characteristics of the method

Analyte	LOD [a]	LOQ [b]	LR [c]	r^2 [d]	RSD% [e]						ER ± SD [f]
					Intra-day precision at the concentrations of (ng mL^{-1})			Inter-day precision at the concentrations of (ng mL^{-1})			
					5	25	50	5	25	50	
Tetracycline	0.26	0.80	0.80-200	0.998	4.9	4.1	3.9	5.6	4.3	4.1	74 ± 4

a) Limit of detection (ng mL^{-1}). b) Limit of quantification (ng mL^{-1}). c) Linear range (ng mL^{-1}). d) Coefficient of determination. e) Relative standard deviation. f) Extraction recovery ± standard deviation (n=3)

Matrix Effect Investigation and Real Sample Analysis

The analytical performance of the developed method was assessed by applying it to the determination of tetracycline in spiked urine samples. Samples were fortified with tetracycline at three concentration levels (5, 10, and 50 ng mL^{-1}) and subjected to the optimized extraction procedure. Relative recovery (RR) values, calculated as the ratio of the peak area obtained from spiked real samples to that from standard solutions, ranged from 96% to 107%. These findings confirm that the sample matrix does not significantly affect extraction efficiency, indicating good method reliability for complex samples. Analysis of unspiked samples revealed no detectable tetracycline residues above the LOD, confirming the absence of background contamination.

Table 2. Investigation of matrix effects in real samples

Sample	Mean relative recovery ± standard deviation (n=3)
	Tetracycline
All samples were spiked with each analyte at a concentration of 5 ng mL^{-1}.	
Urine #1	96 ± 2
Urine #2	101 ± 5
Urine #3	102 ± 4
All samples were spiked with each analyte at a concentration of 10 ng mL^{-1}	
Urine #1	105 ± 4
Urine #2	98 ± 2
Urine #3	103 ± 4
All samples were spiked with each analyte at a concentration of 10 ng mL^{-1}	
Urine #1	99 ± 4
Urine #2	99 ± 2
Urine #3	107 ± 4

Comparison of the Proposed Method with Similar Studies

The analytical performance of the developed method was compared with previously reported techniques for tetracycline determination [26–28], with results summarized in Table 3. The proposed method demonstrates superior or comparable performance in key metrics, including sensitivity (LOD = 0.26 ng mL^{-1}), extraction recovery (74%), linear range (0.8–200 ng mL^{-1}), and precision (RSD < 5.6%). These findings highlight the competitive capability and strong analytical validity of the present method.

Table 3. Proposed method evaluation by comparing similar studies

Method	Sample	LOD [a)]	LOQ [b)]	LR [c)]	RSD % [d)]	Reference
DES–DLLME–HPLC–DAD [e)]	Milk	1.5-8.5	5.1-28.4	5.1-200	0.8-1.7	[26]
SM–LPME–HPLC–DAD [f)]	Egg, milk, and honey	0.7–3.0	2.3–9.9	3–1000	3.1–6.6	[27]
SPE–HPLC–FLD [g)]	Honey	8	25	25–500	≤ 11	[28]
DT-DSPE–HPLC–DAD [h)]	Urine,	0.26	0.8	0.8–200	3.9–5.6	This work

a) Limit of detection (ng mL^{-1})
b) Limit of quantification (ng mL^{-1})
c) Linear range (ng mL^{-1})
d) Relative standard deviation
e) Deep eutectic solvent based–dispersive liquid–liquid microextraction–high performance liquid chromatography–diode array detector
f) Supramolecular–liquid phase microextraction–high performance liquid chromatography–diode array detector
g) Solid phase extraction–high performance liquid chromatography–fluorescence detection
h) Density tunable dispersive solid phase extraction–high performance liquid chromatography–diode array detector

Conclusions

A novel DT-DSPE-HPLC-DAD method using safranal as an innovative sorbent was successfully developed for tetracycline determination in urine. Optimized parameters included dispersive solvent type and volume, sorbent mass, ionic strength, and microwave conditions. The method exhibited excellent analytical performance: LOD (0.26 ng mL^{-1}), linear range (0.8–200 ng mL^{-1}), precision (RSD ≤ 5.6%), and recovery (74%). Effective matrix interference mitigation enabled accurate quantification in spiked real samples. Advantages over traditional SPE include simplicity, speed, reduced solvent use, and high enrichment. However, chloroform toxicity remains a limitation, warranting future exploration of greener alternatives.

Conflict of Interest: Authors declare there is no conflict of interest.

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الاستخلاص الميكروي بالطور الصلب المشتّت القابل لضبط الكثافة بمساعدة الموجات الدقيقة لتقدير التتراسيكلين في عينات البول تمهيدًا لتحليله باستخدام الكروماتوغرافيا السائلة عالية الأداء المقترنة بكاشف مصفوفة الثنائيات

عبير قيس عبدالوهاب

الملخص

في هذه الدراسة، تم تطوير تقنية جديدة وصديقة للبيئة لتحضير العينات، أُطلق عليها الاستخلاص الميكروي بالطور الصلب المشتّت القابل لضبط الكثافة بمساعدة الموجات الدقيقة، وذلك لاستخلاص التتراسيكلين وتركيزه من عينات البول البشري قبل تقديره باستخدام الكروماتوغرافيا السائلة عالية الأداء المقترنة بكاشف مصفوفة الثنائيات. تعتمد الطريقة على استخدام مادة ماصّة عضوية منخفضة الكثافة هي السافرنال، تُذاب في مذيب مشتّت متطاير ثم تُحقن بسرعة في العينة المائية. وعند تعريض المزيج للموجات الدقيقة، يحدث تبخر فوري للمذيب المشتّت، مما يؤدي إلى تكوّن قطرات دقيقة من المادة الماصّة وتشتتها تجانسياً داخل العينة دون الحاجة إلى التحريك الميكانيكي. ونظراً لأن كثافة المادة الماصّة أقل من كثافة الماء، فإن الطور الغني بالمحلَّل يطفو تلقائياً إلى السطح، مما يتيح جمعه بسهولة وسرعة. وقد دُرست العوامل المؤثرة في كفاءة الاستخلاص بصورة منهجية وتمت مواءمتها، وشملت نوع وحجم المذيب المشتّت، وكتلة المادة الماصّة، وقدرة الموجات الدقيقة وزمن التعريض، وكذلك القوة الأيونية. وتحت الظروف المثلى، أظهرت الطريقة أداءً تحليلياً ممتازاً، إذ بلغ حد الكشف 0.26 نانوغرام/مل، مع خطية واسعة ضمن المدى 0.8–200 نانوغرام/مل، ومعامل تحديد لا يقل عن 0.994، واسترجاع استخلاص بلغ 74%. كما كانت الدقة، معبَّراً عنها بالانحراف المعياري النسبي، أفضل من 5.6%. وتم تقييم قابلية تطبيق الطريقة بتحليل عينات بول حقيقية مدعّمة، إذ تراوحت قيم الاسترجاع النسبي بين 96% و107%، مما يؤكد غياب التأثيرات المصفوفية الملحوظة. وبصورة عامة، توفر هذه الطريقة استراتيجية تحليلية سريعة وبسيطة وصديقة للبيئة، تتميز بحساسية عالية وقابلية جيدة لإعادة الإنتاج، مما يجعلها بديلاً واعداً للرصد الروتيني لمتبقيات المضادات الحيوية في المصفوفات الحيوية المعقدة.