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Mutual Derivatization in the Determination of Dapsone and Thymol Using Cloud Point Extraction Followed by Spectrophotometric Detection

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A procedure for the mutual derivatization and determination of thymol and Dapsone was developed and validated in this study. Dapsone was used as the derivatizing agent for the determination of thymol, and thymol was used as the derivatizing agent for the determination of Dapsone. An optimization study was performed for the derivatization reaction; *i.e.*, the diazonium coupling reaction. Linear regression calibration plots for thymol and Dapsone in the direct reaction were constructed at 460 nm, within the concentration range of 0.3-7 μg ml^{-1} for thymol and 0.3-4 μg ml^{-1} for Dapsone, with limits of detection 0.086 and 0.053 μg ml^{-1}, respectively. Corresponding plots for the cloud point extraction of thymol and Dapsone were constructed at 460 nm, within the concentration range of 0.1-2 μg ml^{-1} for thymol and 0.1-1.8 μg ml^{-1} for Dapsone, with limits of detection 0.0445 and 0.023 μg ml^{-1}, respectively. Correlation coefficients and molar absorptivities were improved using cloud point extraction. The proposed method can be applied for their trace detection in different matrices.

Keywords: Cloud point extraction, Dapsone, Derivatization, Extraction, Thymol

INTRODUCTION

Antibacterial agents and biocides are designed to manage unwanted organisms in agricultural and urban environments [1]. Dapsone (4,4-diaminodiphenylsulfone) is a synthetic sulfone with antiseptic activity that it is employed as an antibiotic in animals to treat and prevent diseases [2]. Thymol, a naturally occurring phenol, is an isomer of carvacrol and monoterpene derivative of cymene. Due to its medicinal properties [3], such as the anti-inflammatory, antioxidant, antimicrobial, and antifungal properties, it is added to a wide variety of products including cosmetics, pharmaceuticals, and mouthwashes [4]. With the widespread use of these prescribed drugs, modern analytical methods have become an important requirement for the research on these materials [5,3].

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New approaches to increase the sensitivity and selectivity in addition to lowering the detection limit of analytical procedures often include further steps such as sample pre-treatment and derivatization prior to sample analysis [6]. Sample preparation is a bottleneck and the most significant step in most analytical techniques [7]. Accordingly, sample preparation strategies for the specific and selective extraction of targets, using easy and cost-efficient techniques, are readily available [6] to concentrate the analyte of interest and eliminate the potential interferents [8].

Derivatizations with one or two specific reagents are carried out with the purpose of obtaining a new compound with favourable analytical characteristics. Choice of derivatization agent(s) varies depending on the analytical method, sample matrix and the nature of the analyte [9]. Sample pre-treatment strategies are often coupled with derivatization methods [10].

Spectrophotometric methods are the most popular and attractive methods used recently because of their desirable characteristics such as simplicity, selectivity, specificity, low-cost, common availability and compactness [11,12]; this is in contrast to other techniques, such as high performance liquid chromatography [2] and electrochemical [13] techniques which are high-cost, time-consuming and laborious [14].

The drawback of using an extraction technique such as liquid-liquid extraction (LLE) is the requirement for large quantities of organic solvents, which are flammable, volatile and, most notably toxic and harmful to the environment [15]. Generally, solid-phase extraction (SPE) methods require multiple processing steps requiring much time in addition to their relatively high cost [16].

Micellar systems, such as cloud point extraction (CPE) as the sample pre-treatment and pre-concentration step, combined with spectrophotometric detection, have been highly recommended [17]. It has advantages of low cost, high pre-concentration efficiency and low toxicity [18].

The aim of this study is to use the pre-treatment step, CPE, and derivatization of the analytes by specific and sensitive reactions between the aniline and phenol through the diazonium coupling reaction. The novelty of this work comes from using mutual derivatization of one analyte with the other. Thymol is used as a reagent in Dapsone analysis, and Dapsone is used as a reagent in the determination of thymol. In diazonium coupling, azo chromophores are prepared by diazotization of a primary aromatic amine; *i.e*., the Dapsone, followed by a coupling reaction of the resultant diazonium salt with an electron-rich nucleophile [19,20], *i.e*., thymol. Coupling with phenols needs alkaline conditions, and diazonium salt formation for anilines needs acidic conditions. The resulting azo chromophores have high extinction coefficients [20].

EXPERIMENTAL

Chemicals and Equipment

All chemicals used were of analytical reagent grade with high purity. Sodium nitrite, phosphoric acid, sodium hydroxide, urea, thymol analytical standard and Dapsone VETRANAL™ analytical standard were purchased from Sigma-Aldrich (Baghdad, Iraq). Double distilled water was used throughout the experiments for the preparation of the reagents and samples.

For all absorbance measurements, a double beam dual chopper UV-Vis spectrophotometer, provided with a Czerny-Turner 0.28 m monochromator, Varian, Cary 100, (Mulgrave, Victoria, Australia) was used. A PHS-3E pH meter, Ray Magnetic Instrument Factory, (Shanghai, China) and Mettler digital balance laboratory scale model AE200-200 (Derwood, MD, USA) were also used.

General Procedures

The primary arylamine, 0.1 ml of 2 mM Dapsone, was treated with 0.06 ml of 144 mM sodium nitrite in the presence of 0.12 ml of 12 mM phosphoric acid solution at 0 °C-5 °C using a cooling ice bath for 10 min to form a diazonium salt [21]. Then, 0.1 ml of 660 mM urea was added. The mixture was shaken well and then left to stand for a few minutes, followed by the addition of 0.15 ml of 2 mM thymol and 0.2 ml of 4460 mM sodium hydroxide. The orange colour completely developed immediately. The contents of the flasks were diluted to 10.0 ml with distilled water [19]. For the CPE procedure, 2.0 ml of 10% Triton X-100 was added to a 10 ml derivatization reaction aliquot in 15 ml centrifuge tubes. The tightly sealed (to avoid evaporation) tubes were transferred to a water bath at 95 °C for 30 min until full separation was achieved. In order to increase the viscosity, the tubes were transferred to an ice bath, and the cloudy layer appeared after 3 min. The aqueous phase was decanted, and the cloudy layer remained in the bottom of the tubes [15]. The cloudy layer was clarified at 60 °C in a water bath, then 0.5 ml of it was mixed with 0.5 ml absolute ethanol. Absorbance was measured at 460 nm against a blank consisting of all components except the analyte. Stoichiometry was determined using the Job method of continuous variation (Supplementary, Fig. F) and a molar ratio method (Supplementary, Fig. G). In the Job method, identical concentrations of Dapsone and thymol were used and mixed in varying volume ratios, keeping the total volume constant. In the molar ratio method, a series of samples was prepared, in which the concentration of thymol was kept constant while Dapsone concentration was varied. The absorbance of these mixtures is measured at a suitable wavelength against an appropriate blank solution.

Analysis of Thymol in Mouthwash Products

Thymol was determined in different samples of mouthwashes. The samples were analyzed, without pre-treatment, according to the proposed method; samples were diluted if thymol concentrations were above the linearity range. The samples were determined by the general derivatization and also by the CPE procedure. Spiked samples were prepared for recovery determination by adding 0.5 ml of 10 μg ml^{-1} of thymol.

Analysis of Dapsone in Commercial Tablets

Dapsone powder, 50 ± 0.01 mg from a tablet, was accurately weighed and transferred to a 100 ml volumetric flask and dissolved in 0.01 mM hydrochloric acid. The flask was vortexed for 15 min. Dapsone in aliquots was determined using the proposed method.

RESULTS AND DISCUSSIONS

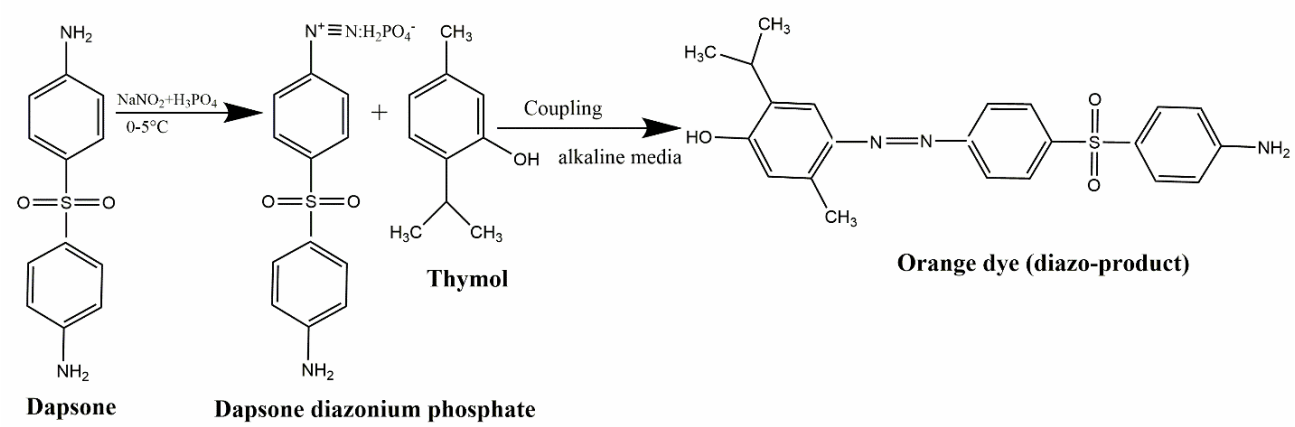
Two different methods were validated and optimized in the determination of Dapsone and thymol, the direct method including the derivatization reaction; *i.e*., diazonium coupling reaction (Scheme 1), and the extraction method, whereby the analytes of the coupling reaction were concentrated by CPE. The optimal parameters of derivatization reaction included the type of acid, acid concentration, sodium nitrite concentration, base type and base concentration. Further optimization steps for the CPE method were surfactant type, surfactant volume, incubation temperature and incubation time. Three replicates were performed for each experiment to determine the standard error for each result, and the error bars are shown in the figures.

Derivatization Reaction Optimization

The stoichiometry determination was achieved using the Job method and mole ratio method (Supplementary Figs. F and G). The selected volume fraction ratio was 0.6 which means the equimolar thymol and Dapsone ratio did not give the highest absorbance, rather, excess thymol (1.5:1.0) had the greatest effect in coupling with the diazonium salt of Dapsone.

Diazonium coupling starts with the formation of nitrous acid by the reaction between sodium nitrite and acid [19]. The acid type and concentration are the essential factors in obtaining a high concentration of nitrous acid that leads to a high concentration of the diazonium salt which was significant in higher light intensity of the coupling product [21]. The acids optimized are nitric acid, sulphuric acid, hydrochloric acid and phosphoric acid (data are shown for 10 mM of acids in Supplementary Material, Fig. A). The reaction conditions at all stages of the procedure are given in the figure captions. The optimum acid chosen was phosphoric acid because it gave the highest absorbance. Since the mechanism of diazotization involves attacking the nitrosating species to the free amine and not the amine salt, it is often necessary to choose a higher acid strength in order to complete the diazotization of weakly basic amines such as nitroanilines and trihalogenoanilines [22]. For the acid concentration study, the other conditions were as in the preceding study. The increase of the acid concentration was effective in increasing the absorbance; the optimum concentration was 12 mM. At the low acid concentrations, the absorbance was low, possibly, because the quantity of acid was not enough to obtain the nitrous acid concentration required to achieve the optimum diazotization, whereas at high acid concentrations, the activity of the primary amine was decreased [23] or an interference may lead to low absorbance [20].

The effect of sodium nitrite concentration was studied with the previously optimized acid type and concentration and the same concentrations of Dapsone and thymol, Fig. 2, from which a sodium nitrite concentration of 0.87 mM was chosen as the optimum. That absorbance was decreased in the upper and lower ranges, might be due to the interferences existing at high concentrations and the insufficient amount of nitrous acid formed at low concentrations of sodium nitrite [24]. Phenolic compounds were used as the active compounds that react with diazonium salts under alkaline conditions [20], thymol in this case. The optimum base was chosen to be sodium hydroxide when compared to potassium hydroxide, sodium carbonate and ammonia (data given in Supplemental, Fig. B for bases other than NaOH). Sodium hydroxide concentration variation showed the optimum of 89 mM. The absorbance was directly proportional to the sodium hydroxide concentration until the optimum point, but decreased after the optimum point that might be due to the



Scheme 1. The proposed mechanism of derivatization reaction

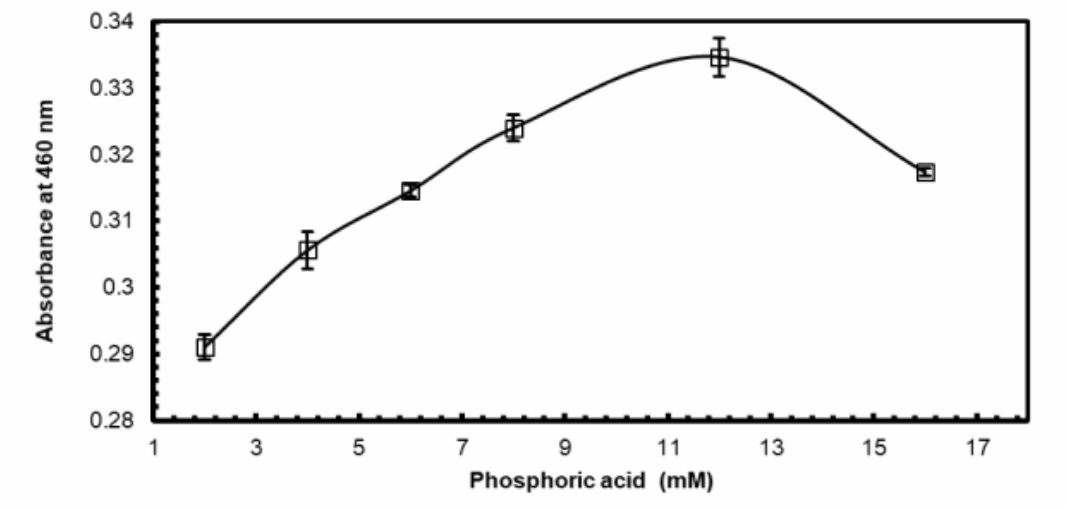


Fig. 1. Phosphoric acid optimization. Conditions: 0.02 mM Dapsone, 1.44 mM sodium nitrite, 6.6 mM urea, 0.03 mM thymol and 44.6 mM KOH.

dilution effect or the interference resulting from diazonium salt alkaline [19,20].

Extraction Optimization

In order to achieve a good selectivity and low detection limit, further pre-treatment and preconcentration experiments were accomplished using a micellar-aided extraction method. Extraction was carried out with the optimized derivatization reaction solution. The distribution coefficient (D) was the parameter used in determining the optimum surfactant and surfactant concentration. The distribution coefficient was calculated by dividing the concentration of thymol in the organic phase by the concentration of thymol in the aqueous phase. Optimizing the surfactant and its concentration were necessary to improve the extraction and pre-treatment step. Triton X-100 was chosen as the best surfactant in the list ranked: Triton X-100 > Tween 80 > hexadecyltrimethylammonium bromide (CTAB) > Tween 20 (data in Supplementary Material, Fig. C). Since the cloud point (CP) is an important

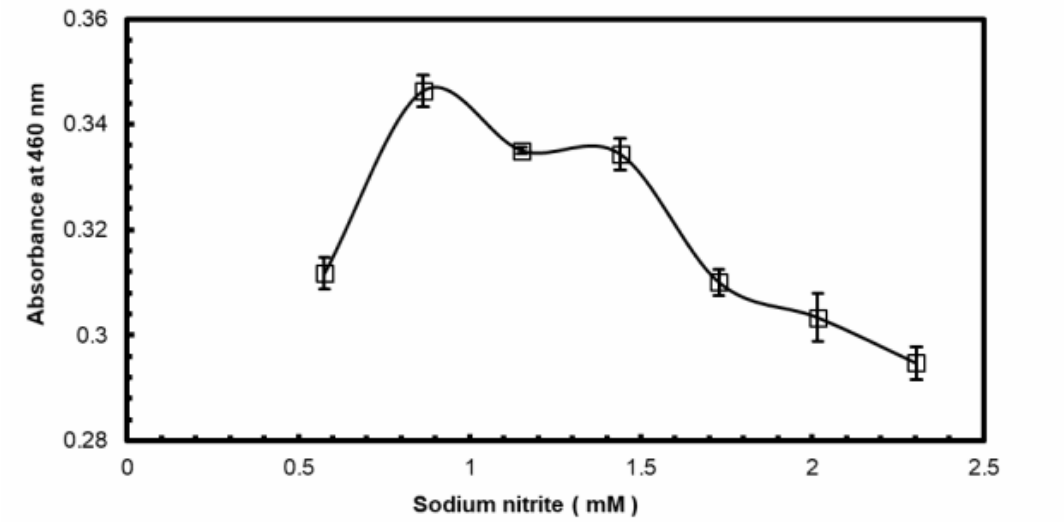


Fig. 2. Sodium nitrite optimization. Conditions: 0.02 mM Dapsone, 6.6 mM urea, 0.03 mM thymol and 44.6 mM KOH, 12 mM H_3PO_4.

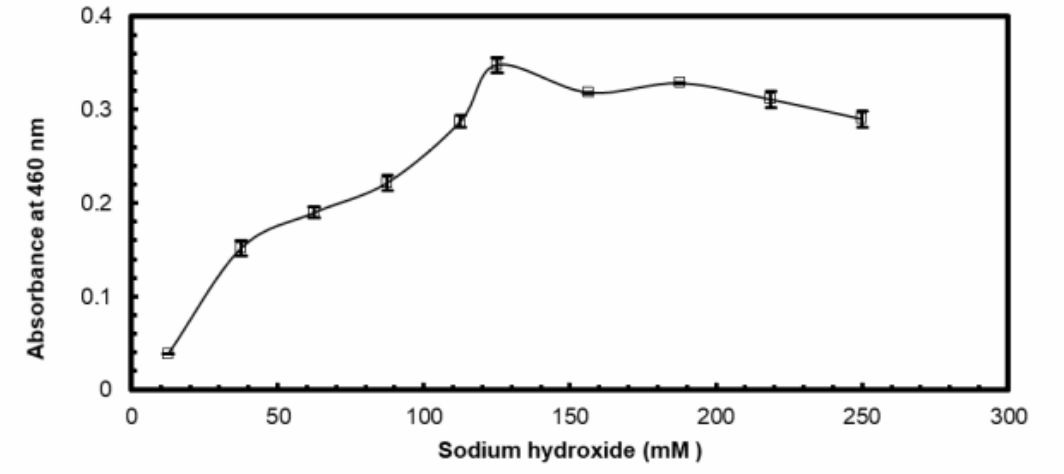


Fig. 3. Sodium hydroxide optimization. Conditions: 0.02 mM Dapsone, 6.6 mM urea 0.03 thymol, 12 mM H_3PO_4, 0.864 mM sodium nitrite.

nonionic surfactant property [25], the surfactants used were nonionic, with the exception of CTAB [26]; CTAB's steric or quaternary ammonium effect [27] offers CTAB superiority over Tween 20.

In the optimization study for the surfactant concentration, the optimum concentration was 1.67%, Fig. 4. The extreme points of show low D values, that might be due to the insufficient surfactant to achieve full extraction at low concentrations, while at high surfactant concentrations, sample dilution could be responsible. Triton X-100 is soluble in water and is the most polar organic solvent among the evaluated surfactants [28].

Full equilibration between the aqueous and organic phases is needed to achieve a high distribution coefficient of

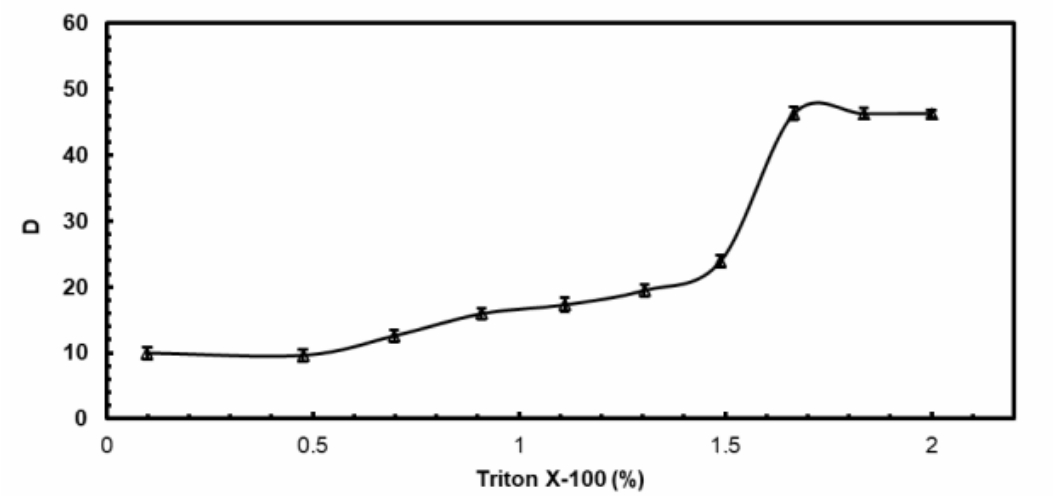


Fig. 4. Triton X-100 optimization. Conditions: 10 ml aqueous phase from optimal derivatization, 25 min extraction time, 90 °C extraction temperature (aqueous phase from optimized coupling in the direct reaction). The aqueous phase components were 0.02 mM Dapsone, 6.6 mM urea 0.03 thymol, 12 mM H_3PO_4, 0.864 mM sodium nitrite and 89 mM sodium hydroxide.

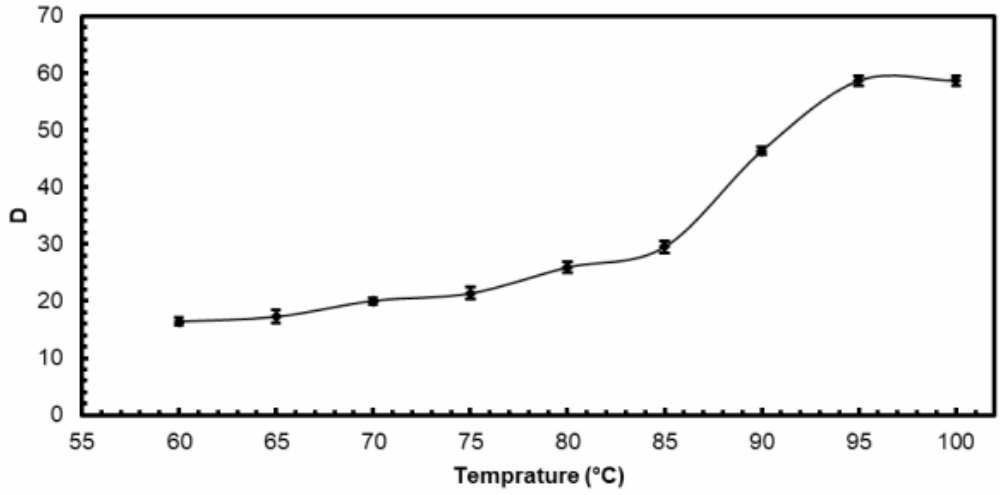


Fig. 5. Temperature optimization. Conditions: 10 ml aqueous phase from optimal derivatization, 1.7% TX-100, 25 min extraction time, (aqueous phase from optimized coupling in the direct reaction). The aqueous phase components were 0.02 mM Dapsone, 6.6 mM urea 0.03 thymol, 12 mM H_3PO_4, 0.864 mM sodium nitrite and 89 mM sodium hydroxide.

extraction [29]. To achieve this, temperature and incubation time were optimized. An incubation time of 30 min was selected as the best time, Fig. 5. At incubation times longer than the optimum time, the distribution coefficient declined, that might be due to the decomposition of the azo dye [30]. Temperature variation, Fig. 6, showed 95 °C as the best

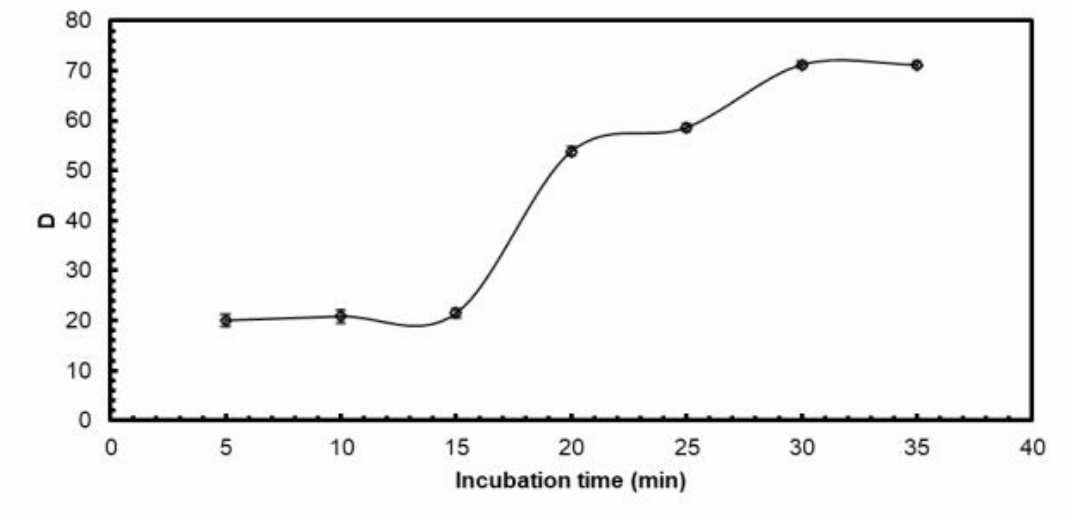


Fig. 6. Incubation time optimization. Conditions: 10 ml aqueous phase, 1.67% TX-100, 95 °C extraction temperature (aqueous phase from optimized coupling in the direct reaction). The aqueous phase components were 0.02 mM Dapsone, 6.6 mM urea 0.03 thymol, 12 mM H_3PO_4, 0.864 mM sodium nitrite and 89 mM sodium hydroxide.

Table 1. Slope, Intercept, Linear Range, Correlation Coefficient, LOD and LOQ[a] of Thymol and Dapsone

Target compound	Slope absorbance ($\mu g\ ml^{-1}$)	Intercept ($\mu g\ ml^{-1}$)	Correlation coefficient r	Linear range ($\mu g\ ml^{-1}$)	LOD ($\mu g\ ml^{-1}$)	LOQ ($\mu g\ ml^{-1}$)
		Derivatization reaction				
Thymol	0.048 ± 0.0008	0.0073 ± 0.003	0.9987	0.3-7	0.086	0.284
Dapsone	0.077 ± 0.0006	0.026 ± 0.001	0.9997	0.3-4	0.053	0.177
		CPE				
Thymol	0.28 ± 0.004	-0.018 ± 0.004	0.9993	0.1-2	0.0449	0.148
Dapsone	0.54 ± 0.01	-0.03 ± 0.01	0.9985	0.1-1.75	0.0229	0.075

[a]LOD = Limit of detection, LOQ = Limit of quantitation.

temperature for extraction. Temperatures higher than the optimum point did not give an increase in the extraction, possibly due to the maximum extraction capacity being achieved [29]. The solution with nonionic surfactant becomes cloudy at the cloud temperature and above, thus, the sample can be separated into two immiscible phases; one of them is a surfactant phase with a low volume that includes the micellar form of the analyte, and the other phase is the aqueous dilute phase [17]. The proposed linearized and optimized method can be applied for sample analysis. Derivatized Dapsone can be analyzed in excess thymol, and the derivatized thymol can be analyzed in insufficient Dapsone. The reagent blank mitigates any effect of the inequivalent amounts of thymol and Dapsone.

Table 2. Comparison of the Current Spectrophotometric Method with other Spectrophotometric Coupling Partners and their Conditions

Reagent	Linear range ($\mu g\ ml^{-1}$)	Molar absorptivity ($M^{-1}\ cm^{-1}$)	Remarks	Ref.
Thymol				
4-Aminoantipyrine	1.0-14	1.966×10^4	Reaction at 0 °C for 2 h	[31]
2,4-Dichloroaniline	1.0-10	2.3×10^4	Reaction at 0 °C	[32]
2,6-dichloroquinone-4-	0.04-16	18430	pH 10 at room temp.	[33]
2,4-Dinitrophenylhydrazine	10-150		Reaction at 25 °C	[34]
2,4-Dinitrophenylhydrazine	0.25-10	2.2×10^4	Reaction time 15 min	[35]
Proposed method	0.1-2.0	1.44×10^4		
Dapsone				
Phloroglucinol	0.4-10	4.79×10^4	Reaction at 0 °C for 3 min	[36]
Pyrocatechol	0.4-20	1.05×10^4	Reaction at room temp. for 2 min	[37]
4-Nitrophenol	3.0-50	3.58×10^3	55 °C for 20 min, pH 2	[38]
1,2-Naphthoquinone-4-	0.40-10	3.68×10^4	pH 9.8	[39]
Proposed method	0.1-1.8	1.9×10^4		

Table 3. Accuracy, Precision and Determination of Thymol and Dapsone in Dosage Forms

Drug form	Proposed methods					
	Direct			CPE		
	Conc. ($\mu g\ ml^{-1}$)[a]	Recovery (%)[a]	RSD (%)[a]	Conc. ($\mu g\ ml^{-1}$)[a]	Recovery (%)[a]	RSD (%)[a]
	Thymol					
Listerine	186	100.6	0.42	186	100.9	0.41
Lacalute	3377	99.7	0.49	337	101.2	0.39
	Dapsone					
Dapsone by Fouda (Egypt)	302	100.7	0.39	306	101.9	0.36
Dapsone by + SGpharma (India)	302	100.7	0.39	305	101.7	0.35

[a]Average of three replicates at the concentrations shown.

Calibration Curves and Validation Study

Calibration curves were constructed for Dapsone and thymol for the method before and after the extraction steps (Table 1; Supplementary, Figs. D and E).

The molar absorptivities of Dapsone and thymol using the CPE method (81118 ± 2500 and 41610 ± 500 $M^{-1}\ cm^{-1}$, respectively) were higher than those using the direct method (19100 ± 150 and 14451 ± 119 $M^{-1}\ cm^{-1}$, respectively). The limits of detection (LOD) of the Dapsone and thymol using the CPE method (0.0229 and 0.0449, respectively) were lower than those of the direct method (0.053 and 0.086, respectively) indicating the improvement of CPE method

due to the efficiency of the extraction step. The accuracy and precision were calculated for both methods for both drugs. Average of RSDs of five replicates of three selected concentrations (0.3, 0.7, 1.75 μg ml^{-1}) were used to calculate the precision. The precision was lower than 0.5 (RSD% < 0.5), while the accuracies were in the range 100.4-100.7% (Table 1). The table also shows the proposed methods to be in good accord with previous studies of other coupling partners.

Analytical Application

The proposed derivatization method at trace levels was achieved without requiring pH control or extreme temperature in comparison with some previous studies (Table 2).

In comparison with the direct method, the CPE procedure is more convenient than the former method because of its selectivity, low detection limit (Table 1) in addition to high molar absorptivity. Because of matrix effect and high concentrations of the mouthwash ingredients, use of the CPE procedure was essential.

The precision of the methods was evaluated by analysing pure samples of thymol and Dapsone, and good recoveries were obtained by analysing the marketed formulations in pentaplicate (Table 3). As the RSDs show, these determinations were reproducible within 0.5%.

Finally, statistical analyses by the F- and T-tests reveal that there is no significant difference in the precision and accuracy between the proposed method and official spectrophotometric methods. The method could be readily extended to other anilines or phenols that can be mutually coupled. Due to the selectivity characteristics of the derivatization-extraction method, it could also be applied for the analysis of thymol and Dapsone in environmental samples and wastewater.

To evaluate the selectivity of the proposed methods for the analysis of pharmaceutical preparations containing Dapsone and mouthwash containing thymol, the interfering effect of excipients or other components were examined by determining Dapsone and thymol in the presence of potential interferents. The excipients studied were lactose, talc, starch, magnesium stearate and polyvinylpyrrolidone in the interference test of Dapsone; the other components of mouthwash were benzoic acid, sodium benzoate, methyl salicylate and chlorhexidine digluconate. For this study, solution containing Dapsone or thymol and each one of the potential interferents were taken separately in concentrations five-times greater than those of Dapsone or thymol that were analyzed. Under these conditions, none of them interfered in triplicate determinations; RSDs were less than 0.5% (data of recovery% and RSDs% are given in Supplementary Materials, Table A).

CONCLUSIONS

The CPE step has been successfully applied in the determination of drugs by mutual derivatization to improve the analytical procedure by enhancing the sensitivity, selectivity and accuracy. This was achieved through optimizing the conditions of derivatization by azo coupling (base type and concentration were the most important parameters) and optimizing the conditions of micellar extraction of the coupling product (temperature and incubation time were the most important parameters). A low detection limit was achieved due to the extraction step. Moreover, the proposed procedures have a lower cost compared with other methods such as HPLC and GC.

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