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## **A Method Based on Ultrasound-assisted Solidification of Floating Drop Microextraction Technique for the Spectrophotometric Determination of Curcumin in Turmeric Powder**

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A method based on the ultrasound-assisted solidification of floating drop microextraction technique was developed for the spectrophotometric and spectrofluorimetric determination of curcumin in turmeric powder. In this work, a small volume of an organic solvent was floated on the surface of an aqueous solution. After sonication, the organic solvent is solidified and separated. The effect of extraction parameters such as type and the volume of organic solvent, temperature, salt addition and exposure time on the extraction recovery was investigated and optimized. Finally, the droplet method - was used for the determination of analyte. Under the optimum extraction conditions, a linear range of 0.006-3  $\mu\text{g ml}^{-1}$  and a relative standard deviation (RSD) of 2.72% for curcumin were achieved. Detection limits of 7 and 2  $\text{ng ml}^{-1}$  curcumin were obtained for the spectrophotometric and spectrofluorimetric methods, respectively. The obtained results show that the application of this method can be successful for the analysis of curcumin in turmeric powder samples.

**Keywords:** Curcumin, Solidification of floating drop microextraction, Spectrophotometry, Spectrofluorimetry, Turmeric powder

### **INTRODUCTION**

Curcumin ([1,7-bis-(4-hydroxyl-3-methoxyphenyl)-1,6-heptadiene-3,5-dione,  $\text{C}_{21}\text{H}_{20}\text{O}_6$ ,) is a natural polyphenolic compound isolated from the rhizome of *Curcuma longa* Linn [1,2]. Curcumin is commonly used in food products, mainly as coloring agent. Curcumin is a yellow-orange powder insoluble in water but very soluble in organic solvents, such as methanol, ethanol, dimethylsulfoxide, and acetone, and is unstable to light. It has a melting point of 183.8 °C. The maximum absorption of curcumin in methanol is at 430 nm and in acetone at 415-420 nm [3].

Researches have shown that curcumin has a wide range of beneficial biological and pharmacological activities. Curcumin has been proposed as a potential agent against various chronic diseases (Alzheimer's [4] and Parkinson's disease, epilepsy, multiple sclerosis), cardiovascular

diseases (CVD) [5], allergies, obesity, anorexia, antiparasitic, coughs, rheumatism, diabetes and certain types of cancer [6,7]. Quantification of curcumin, the principal curcuminoid of turmeric, is one of fields of science due to its anti-inflammatory, antioxidant and anti-cancerous properties. Different methods have been used for curcumin determination [8]. Different methods have been used for curcumin determination such as spectrophotometry, HPLC and spectrofluorimetry [9-13].

Sample preparation is an essential step in chemical analysis. Recently, the green extraction methods have been developed for this purpose. Even in modern techniques, complete elimination of organic solvents is not always possible [14]. Traditional sample preparation techniques such as liquid-liquid extraction and solid phase extraction are time consuming and/or use large amounts of toxic organic solvents, which may be dangerous to human health and to the environment. Because of these disadvantages, developing of new, fast, inexpensive, environmentally

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friendly and easy to use microextraction techniques have been gaining a growing interest [15]. Analytical methods that employ smaller volumes of initial sample and/or extracting solvent would be preferable. So, miniaturization of the liquid-liquid extraction technique is an attempt to eliminate or minimize these drawbacks [16,19].

Liquid-phase microextraction (LPME) has been developed as an alternative extraction technique [20]. This method provides analyte extraction using only a few microliters of organic solvent. LPME avoids some problems of the SPME method such as fiber degradation; it is also fast, inexpensive and uses very simple equipment.

For the first time, in 2007, Zanjani *et al.* reported a new liquid-liquid microextraction method based on solidification of floating organic drop for the extraction (SFODME) of analytes [21,22]. SFODME is one of the most powerful, rapid and inexpensive techniques for liquid-phase microextraction (LPME). In this method, a small volume of an organic solvent is floated on the surface of an aqueous solution. After the completion of the extraction by sonication, the organic solvent is solidified by placing the vial in an ice bath. Finally, the melted droplet is used for analyte determination by a proper method. The applied organic solvent should have a melting point near the room temperature (10-30 °C), be immiscible with water and should have lower density than water. Then, this method has been also the purpose of many developing research plans. The SFODME is a modified solvent extraction method taking advantages of simplicity, low cost, minimum organic solvent consumption, environmentally friendly and achievement of high enrichment factor. However, the prolonged extraction time [22-26], limited choice of the proper solvent and freezing the extract are of the SFODME technique's drawbacks.

The purpose of this work is investigation of the applicability of SFODME method for the extraction of curcumin from turmeric powder samples prior to its determination by spectrophotometric and spectrofluorometry methods.

## EXPERIMENTAL

### Chemicals and Reagents

All chemicals and reagents used in this work were of

analytical grade and purchased from Merck (Darmstadt, Germany). A curcumin stock solution in methanol (1000 mg l<sup>-1</sup>) was prepared. Working standard solutions were prepared by suitable dilution of the stock solutions. Hydrochloric acid and sodium hydroxide were used for pH adjustments. All solutions were prepared using double-distilled water.

### Apparatus

A single beam UV-mini-WPA spectrophotometer was used for the determination of curcumin concentration in the solutions. A Metrohm model 713 pH-meter was used for pH measurements. Fluorescence measurements were performed with a PerkinElmer (LS50B) luminescence spectrometer with a 1.0 cm quartz cell, slit width = 10 nm, wavelength scan rate = 500 nm min<sup>-1</sup>. A 40 kHz universal ultrasonic cleaner water bath (RoHS, Korea) was also used.

### Extraction Procedure

An aqueous solution of curcumin with the concentration of 0.8 µg l<sup>-1</sup> was used in the optimization studies. A 10 ml of the standard solution was transferred into a 20 ml vial and 8 microliters of 1-dodecanol were placed on the solution surface by a microliter syringe. The vial was sealed and immersed into the ultrasonic bath. When the desired extraction time elapsed, the sample vial was transferred into an ice bath, and then the organic solvent was solidified after 5 min. Finally, 300 microliters of the extractant were transferred into the quartz cuvette for quantification. The solidified solvent was transferred into the conical vial and melted quickly and the melted solvent was diluted with methanol. Finally, extractant drops were transferred into the quartz cuvette for quantification.

### Sampling and Sample Pretreatment

A simple spectrophotometric method was used and the results were satisfactory for the curcumin analysis during the optimization. As curcumin is a fluorescent compound, a calibration curve was also constructed from spectrofluorimetric measurements under the same optimum condition. For doing so, a 100 µg ml<sup>-1</sup> sample of pure curcumin was prepared in methanol. This was scanned spectrofluorimetrically to obtain the excitation and emission wavelengths. The spectra shown by curcumin had an

**Table 1.** Determination of Curcumin in Turmeric Powder, under the Optimized Conditions (The Entire Procedure was Repeated Three Times for each Sample and the Readings were Expressed as Mean  $\pm$  S.D)

Added ( $\mu\text{g ml}^{-1}$ )	Found ( $\mu\text{g ml}^{-1}$ )	Recovery (%)	Independent method (n = 3, $\mu\text{g ml}^{-1}$ )	$t_{\text{exp}}^a$
0.00	0.048 $\pm$ 0.001	-	0.043 $\pm$ 0.002	2.727
0.05	0.097 $\pm$ 0.001	99.0	-	-
2.00	2.014 $\pm$ 0.010	98.3	-	-

<sup>a</sup> $t_{\text{exp}}$  shows the experimental student-t values, ( $t_{\text{critical}} = 2.78$ )

excitation wavelength at 479 nm and an emission wavelength at 529 nm for curcumin and the intensities were recorded. However, a spectrofluorimetric method was used for the final analysis of the turmeric powder samples under consideration. The obtained results of the turmeric powder samples are summarized in Table 1.

A 100 mg turmeric powder was weighed accurately and extracted with 10 ml methanol with vigorous shaking. It was then filtered and the volume made up to 100 ml with methanol. Then, 0.1 ml of this solution was further diluted to 100 ml and analyzed in the spectrofluorimetrically. The concentration of curcumin in the extract sample was determined from the standard curve. All samples were filtered and stored at 4 °C before extraction. The samples were screened to detect curcumin. Therefore, the samples were spiked with a known concentration of curcumin (0.05, 2 mg l<sup>-1</sup>) before its subjecting to the SFODME procedure. Recoveries were calculated and reported for the developed method according to an added-found method.

## RESULTS AND DISCUSSIONS

The different parameters affecting on the partition of the analytes between the organic solvent and the aqueous solution such as the type of organic solvent, organic solvent and aqueous sample volumes, extraction time, stirring rate and salt addition were investigated and optimized using aqueous solutions of 0.8  $\mu\text{g l}^{-1}$  of curcumin.

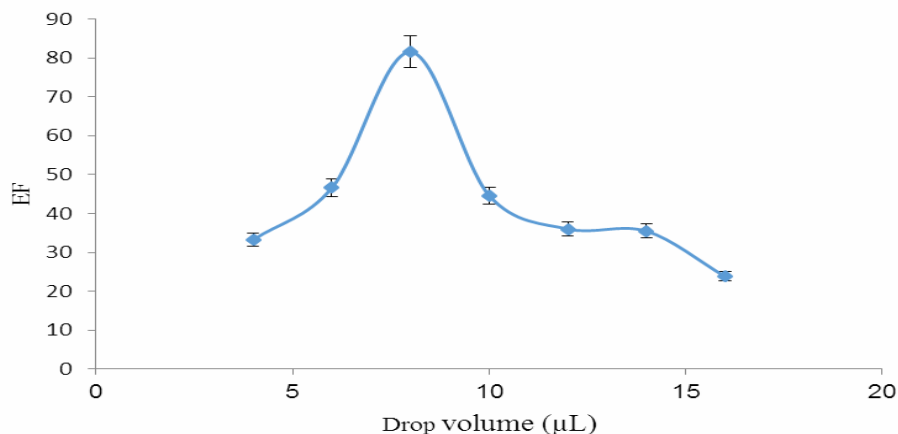
### Organic Solvent and Drop Volumes

Selection of an appropriate extraction solvent is one of the key factors for optimizing LPME process. The extraction solvent should have three requirements: (1) to be immiscible with water and have low volatility in order to be stable at the extraction period, (2) to extract analytes well, (3) to have melting point near the room temperature (in the range of 10-30 °C) [21,27,28].

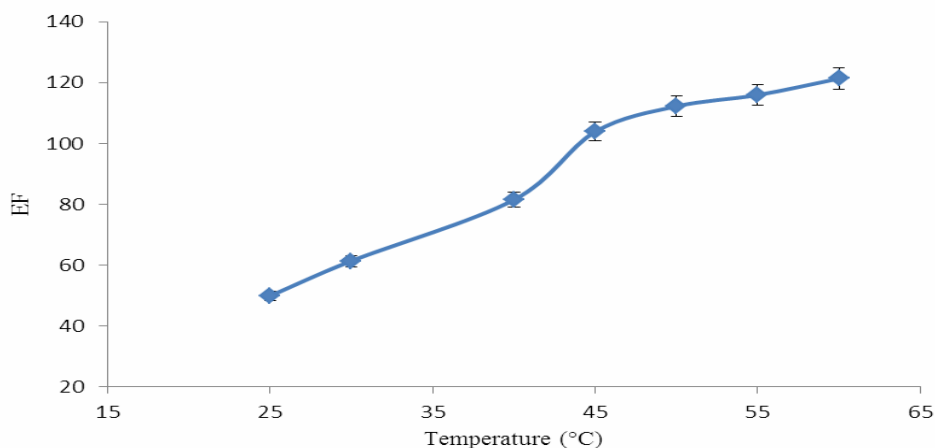
Several types of organic solvents including 1-dodecanol, 1-undecanol, 2-dodecanol and diphenyl ether, were used for extraction of curcumin from turmeric powder. The results showed that 1-dodecanol exhibited high extraction efficiency. Therefore, 1-dodecanol with a melting point of 24 °C was chosen as the organic solvent. To increase the sensitivity of the LPME method, the effect of solvent volume on the extraction efficiency was investigated in the range of 4.0-16.0  $\mu\text{l}$  and optimized. According to Fig. 1, by increasing the microdrop volume to 8  $\mu\text{l}$ , the increase in the extraction efficiency was obtained. However, at larger volumes (*i.e.* > 8  $\mu\text{l}$ ), extraction efficiency increased, while due to dilution effect, curcumin concentration in the organic phase decreased. Organic solvent volume of 8  $\mu\text{l}$  was therefore selected for the subsequent experiments [27].

### Sample Solution Temperature

In the present study, the effect of the solution temperature on the extraction efficiency was studied in the range of 25-70 °C (Fig. 2). The results showed that



**Fig. 1.** The influence of the drop volumes on the enrichment factor of curcumin in the SFODME method. Experimental conditions: the stirring rate: 50 rpm; sample volume, 10 ml; temperature: 40 °C ; extraction time: 30 min.



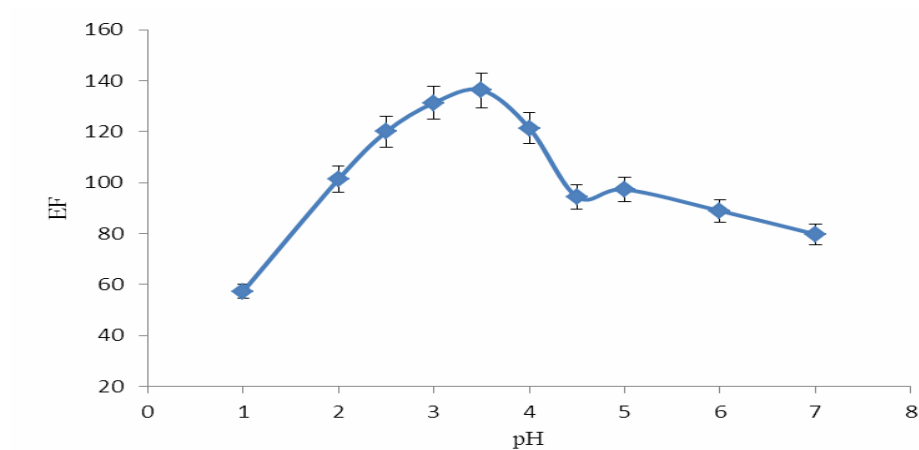
**Fig. 2.** The influence of the temperature on the enrichment factor of curcumin in the SFODME system. Experimental conditions: the stirring rate:50 rpm ; sample volume, 10 ml; volume of organic solvent, 8 µl ; extraction time, 30 min .

extraction efficiency increased by rising temperature. Solution temperature affects the extraction kinetics. At higher temperatures diffusion coefficients and mass transfer of analytes from sample to the organic solvent increased and the time required to reach equilibrium decreased [28]. Therefore, with utilizing higher temperatures at lower extraction times, equilibrium was obtained faster and higher extraction efficiencies were achieved. At higher temperatures (> 60 °C), the over-pressurization of the

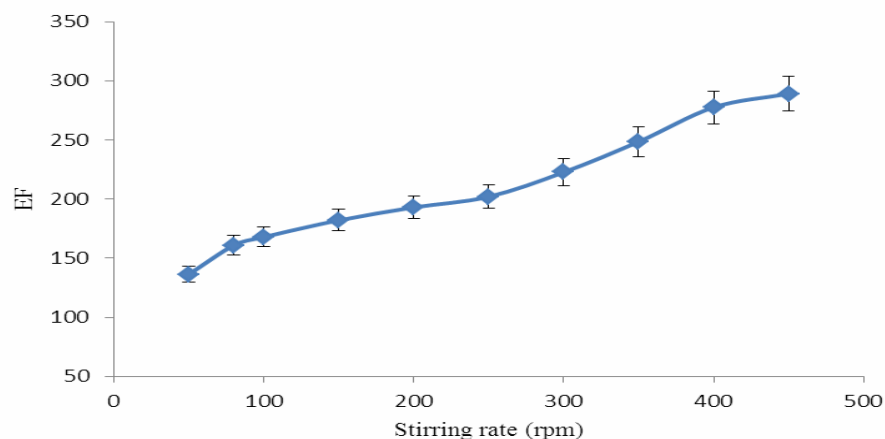
sample vial made the extraction system unstable. Thus, in the further experiments, the sample vial temperature was held at 60 °C. Thus, optimum temperature of 60 °C is valid only for the extraction time used in the experiment.

### Sample pH

Curcumin appears brilliant yellow color at pH 2.5-7.0 and red at pH > 7.0. It can exist at least in two tautomeric forms, keto and enol. By varying the pH of the solution,



**Fig. 3.** The influence of the sample pH on the enrichment factor of curcumin in the SFODME system. Experimental conditions: the stirring rate, 50 rpm; sample volume, 10 ml; volume of organic solvent, 8  $\mu$ l; extraction time: 30 min; temperature: 60  $^{\circ}$ C.



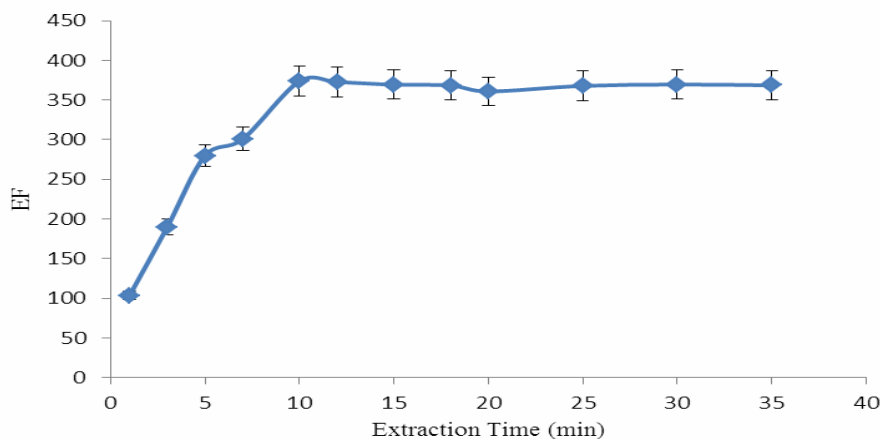
**Fig. 4.** The influence of the stirring rate on the enrichment factor of curcumin in the SFODME system. Experimental conditions: sample pH, 3.5; sample volume, 10 ml; volume of organic solvent, 8  $\mu$ l; extraction time, 30 min; temperature, 60  $^{\circ}$ C.

curcumin exists in different forms. Usually, curcumin is stable at acidic pHs but unstable at neutral and basic pHs, which is degraded to ferulic acid feruloylmethane [30]. Thus, the pH of 3.5 was chosen for the subsequent extractions (Fig. 3).

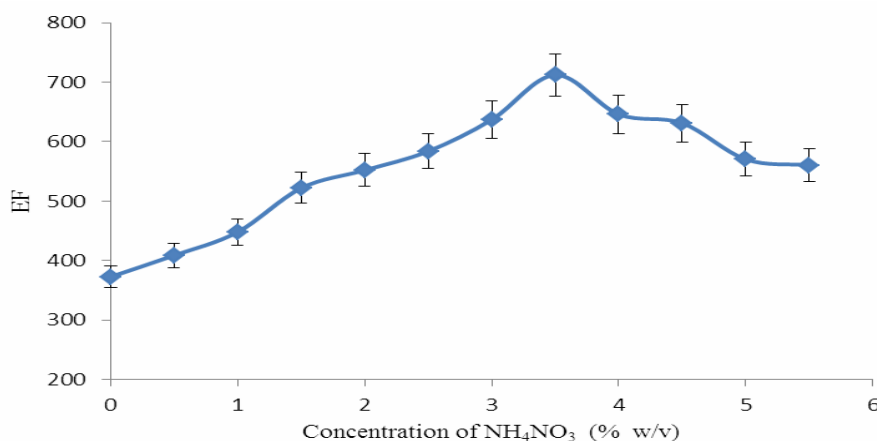
#### Effect of the Agitation Method

Sample agitation has a great role to enhance extraction efficiency and to reduce extraction time [28]. In this work,

the samples with a volume of 10 ml were continuously agitated at different stirring rates (0-450 rpm). According to the results, the recovery increased by increasing the stirring rate up to 450 rpm. Hence, a stirring rate of 450 rpm was employed for further studies. Two different agitation methods of ultra-sonication and magnetic stirring were compared for SFODME method. Therefore, ultra-sonication was selected as the better agitation method. When ultrasonication was used, shorter extraction times were



**Fig. 5.** The influence of the extraction time on the enrichment factor of curcumin in the SFODME system. Experimental conditions: the pH, 3.5; sample volume, 10 ml; volume of organic solvent, 8  $\mu$ l; temperature, 60  $^{\circ}$ C.



**Fig. 6.** The influence of the concentration of NH<sub>4</sub>NO<sub>3</sub> on the enrichment factor of curcumin in the SFODME system. Experimental conditions: Sample pH, 3.5; sample volume, 10 ml; volume of organic solvent, 8  $\mu$ l; extraction time, 12 min; temperature, 60  $^{\circ}$ C.

necessary. Ultrasonic irradiation enhances the rate of mass transfer between two immiscible phases, reduces the equilibrium time and several extraction vials can be stirred simultaneously.

### Extraction Time

The effect of extraction time on extraction efficiency was examined in the range of 1-35 min under ultrasonication. The extraction efficiency increased by

increasing the extraction time up to 10 min. After 10 min, the extraction efficiency remained nearly constant. The extraction time profiles indicated that the equilibrium is achieved after 10 min (Fig. 5). Thus, an exposure time of 12 min was selected for the subsequent experiments [29].

### Salt Addition

Addition of salt into the sample solution can improve the extraction efficiency of the analytes due to salting out

effect. The salting out effect has been widely used in LPME and SPME. However, higher concentrations of salt restrict extraction of the analytes. The presence of higher concentrations of salt changes the physical properties of the extraction film and thus reduces the diffusion rates of the analytes into the organic phase. Seven salts, including  $\text{NH}_4\text{NO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaCl}$ ,  $\text{KNO}_3$ ,  $\text{KCl}$ ,  $\text{NaI}$ ,  $\text{NaNO}_3$ , were tested. The pH of the solution was adjusted at 3.5 after addition of the salt. In the present work, extraction efficiency increased by adding salts at the concentration range 0-5.5% w/v. At higher salt concentrations ( $> 3.5\%$  w/v), the extraction efficiency decreased that may be attributed to the increase in the aqueous solution viscosity and the decrease in the analyte mass transfer from the solution into the organic solvent (Fig. 6). The best results were obtained by  $\text{NH}_4\text{NO}_3$ . Thus, further extractions were carried out at a  $\text{NH}_4\text{NO}_3$  concentration of 3.5% w/v followed by adjusting the pH at 3.5 [27, 31,32].

### Effect of Sample Volume

Effect of sample volume on the extraction of curcumin was investigated in the range of 5.0-30.0 ml. Then, extraction was performed under the optimum conditions described above. It was found that quantitative recovery was obtained for curcumin in sample volumes up to 10 ml.

### Analytical Performances

Calibration curves were provided from spectrophotometric measurements, performed under the optimum conditions described above. The calibration curve was linear in the range of 0.023-2.50  $\mu\text{g ml}^{-1}$ . The calibration equation was  $A = 1.0483C + 0.0183$  with a correlation coefficient of 0.9988 ( $n = 12$ ), where A and C are the absorbance at nm and the curcumin concentration, respectively. The detection limit (DL) was found to be 7  $\text{ng ml}^{-1}$ .

The liner relationship between fluorescence intensity for curcumin and its concentration in extract solution was found to be in the range of 0.006-20.0  $\mu\text{g ml}^{-1}$ , and the calibration equation was  $I_f = 4.2334C + 1.3927$  with a correlation coefficient of 0.9992 ( $n = 12$ ). The linear regression data are listed in Table 2. The detection DL was found to be 2  $\text{ng ml}^{-1}$  for spectrofluorimetric method. The relative standard deviation (R.S.D.) for 0.8  $\mu\text{g ml}^{-1}$  of

curcumin was found to be 2.72% ( $n = 3$ ). The method was validated in terms of linearity, accuracy and precision. Comparison of the characteristics of the calibration curves obtained by spectrophotometry and spectrofluorimetry show that the spectrofluorimetric method provides lower detection limit and wider liner range.

Although spectrophotometric method is simple and cost effective, it is not as enough sensitive as spectrofluorimetry. So, for further studies, the fluorescence method was applied.

As curcumin content in 10 ml of the initial solution was extracted into 1 ml, the maximum enrichment factor was obtained as 10.

### Application

To investigate the applicability of the method in the analysis of real samples, the method was applied to the extraction and spectrofluorimetric determination of curcumin in *turmeric powder*. Dried rhizomes of *Curcuma longa* were obtained from the local markets in Hamadan. The resulting solutions were filtered and subjected to the SFODME process. The sample was also spiked by two different concentrations of curcumin and analyzed by the proposed method and the values of the recoveries were calculated as 99 and 98.3%. The analytical results are presented in Table 1. Table 1 shows a comparison based on t-test at 95% confidence interval, demonstrating that there is not any significant difference between this work and independent method [33]. This indicates that the method is suitable for the determination of curcumin in such samples.

Table 3 shows a comparison between the results obtained by the present method and those obtained by some other methods reported for the determination of curcumin. This comparison shows that analytical performance of the proposed method is comparable with that of some sensitive instrumental method, such as HPLC, and in some cases, the method is not superior on the analytical figure of merit bases. Compared with the traditional separation techniques, the proposed technique does not require large amounts of toxic organic solvents. Compared with other proposed spectrophotometry and spectrofluorometry methods, this method has the higher sensitivity. Compared with the metal complex, this method does not require a large number of

**Table 2.** The Linear Regression Data for the Proposed Method

Parameters	UV-Vis	Fluorescence
Calibration equation	$y = 1.0483C + 0.0183$	$y = 4.2334C + 1.3927$
Liner relationship ( $\mu\text{g ml}^{-1}$ )	0.023-2.50	0.006-20.0
Detection limit ( $\mu\text{g ml}^{-1}$ )	0.0070	0.0020
Determination coefficient ( $R^2$ )	0.9988	0.9992

**Table 3.** Comparison of the Proposed Method with some Previously Reported Methods for Curcumin Determination

Method	LOD ( $\mu\text{g ml}^{-1}$ )	Sample	LDR ( $\mu\text{g ml}^{-1}$ )	RSD	Ref.
DLLME-HPLC <sup>a</sup>	0.005	Serum	0.05-100	2.87	[9]
CPE-UV-HPLC <sup>b</sup>	0.066	Urine	0.22-100	2.7	[10]
UV-Vis	0.280	Turmeric powder	1.0-7.0	0.22	[11]
LC-MS/MS <sup>c</sup>	0.010	Plasma	0.010-2.0	<3.55	[12]
SFODME	0.002	Turmeric	0.006-20.0	2.72	Thiswork

<sup>a</sup>Dispersive Liquid-liquid microextraction. <sup>b</sup>Cloud point extraction. <sup>c</sup>Liquid chromatography-mass spectrometry/mass spectrometry.

heavy metals, reducing heavy metal pollution. Using spectrophotometry and spectrofluorometry can greatly reduce the use of costly equipment and expenses in HPLC and mass spectrometry methods; based on the simple equipment they need, this method more likely could be widely used in real life. However, other advantages of the proposed method are simplicity, less expensive, low LOD,

wide linear range, highly enrichment factor and short extraction time.

## CONCLUSIONS

Solidification of floating drop microextraction was used to the preconcentration of curcumin from aqueous solutions



with high enrichment factor. SFODME is a relatively new sample pre-treatment method combining sampling, extraction, and pre-concentration all together. Compared with traditional extraction methods it has the advantages of simplicity of operation, rapidity, low cost, high recovery and high pre-concentration factor. Under optimum conditions, the spectrofluorometry method is sensitive compared with the HPLC and MS/MS methods. The sensitivity of the proposed spectrophotometry method is also higher than that of other spectrophotometry methods. However, the main drawback of the proposed method is the limitation of selecting an extracting solvent, because just a few organic solvents are close to the melting point of room temperature, as well as overlapping of the solvent peaks with those of the analytes. Since a fresh portion of organic solvent is used for each extraction, there is no memory effect and since the volume of the organic phase is only at few microliter levels, large preconcentration factors are achievable. In addition, SFODME is very simple, low cost and suitable for batch operations, which could greatly shorten the sample preparation time. Also, when ultrasonication was used, highly enrichment factor and short extraction time were monitored. Most of similar methods are time consuming and labor intensive, while the proposed method is very simple, fast and easy to operate using least utilities.

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