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A New Method For Extracting Microfluids Using Droplet Technology

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Abstract: *An innovative and sensitive method for extracting liquid-liquid flour using pre-mixing with the single-drop microextraction technique. This working system is distinguished by its ability to be applied to chemical and biological analyses. It is suitable for microfluidics, has a short time, is free of contaminants, and has a simple design that can be installed anywhere in the laboratory. The working system consists of several basic parts: a pump device to pump or fall back the organic and aqueous phase from the liquid-liquid micro-system through micro-rubber tubes and two precise micro-needles to generate drops, two mixers using two magnetic clamps on two graduated holders, and a precise micro-mixer to complete the mixing process. Study of the main variables in the system containing dithizone (0.0001 M).) in $CHCl_3$ solvent solution and aqueous copper chloride solution (1000 ppm) to see how they affect the extraction performance obtained by this method. The effect of the copper concentration in the initial sample, the speed of the mixer, and the flow rate were discussed and studied, and the best conditions were determined: for (2 ml) sample an aqueous solution of copper (II) chloride, the optimal concentration of copper. (II) in the analyzed sample is (0.0001M), the speed of the micromixer is maximum, and the pump flow rate is (0.5 ml /sec). In these optimal conditions, the degree of extraction was (97±2%).*

Keywords: *Microextraction, droplet technology, droplet premixing system, droplet extraction process, automated droplet extraction, single drop technology.*

1. INTRODUCTION

Separation techniques are extremely important in various chemical and biological analyses .One of them is liquid-liquid extraction techniques, which started with traditional means and equipment until they reached the level of advanced efficiency. The separation efficiency in liquid-liquid extraction techniques depends on thermodynamics, which represents the balance of the two phases, and hydrodynamics, represented by mixing and contact between the two phases and mass transfer, which represents molecular diffusion. A deep understanding of the principles of chemistry and awareness of the principles of green chemistry produced the advanced droplet technology. This technology relies on fine chemistry technology related to droplet behavior, on which the accurate calculation of the size distribution of droplets depends. Currently, many diverse methods have been established for the formation, breakage, and coalescence of droplets, and knowledge of hydrodynamics has increased, which reflects the size of droplet dispersion and the mixing process of the two phases, thus determining the mass transfer contact region. The droplet technology has influenced the liquid-liquid extraction technology and has become a platform of high accuracy and sensitivity through precise control of the equipment, the droplets, and the interface between the two liquids. [1], [2]

2. EXPERIMENTAL

Chemicals

The droplet extraction technique requires small volumes, up to several milliliters at most. It should be noted that some low concentrations require larger volumes, but the actual use of the reagent and metal ion solutions required by the micro-extraction process for the droplet technique is in microliter volumes, so this process requires high accuracy and precision. All chemicals were used in this research by the companies (Fluka and BDH). The dithizone solution ($C_{13}H_{12}N_4S$) (Fluka) was prepared at a concentration of (0.01 mole) by dissolving (0.0256 g) in (10 ml) of hydrogen chloride (BDH). For the purpose of studying the various effects, another group of dithizone solutions was prepared at a concentration of (0.001 mole) by taking (5 ml) of the previous dithizone solution at a concentration of (0.01 mole) and diluting it in (50 ml) of hydrogen chloride in a flask used for standard volumes and it was stored. The solution was kept in a dark bottle away from light to keep the solution from oxidation. An aqueous solution of copper (II) chloride ($CuCl_2.2H_2O$) (Fluka) was prepared with a concentration of (0.01 mole) by dissolving (0.42625 mg) in a small volume of distilled water, then completing the volume to (250 ml) of distilled water in a standard volumetric flask and saving the solution for use. To study the basic changes, another group of copper (II) ion solutions $CuCl_2$ was prepared with a concentration of (0.0001 mole) by taking (0.5 ml) of the previous copper (II) chloride solution with a concentration of (0.01 mole) and diluting it in (50 ml) of distilled water in a standard volumetric flask when the concentration of copper (II) is standard (0.635 ppm) and the acidity of the $CuCl_2$ solution is adjusted to pH = 1, in order to obtain high selectivity. The pH was monitored using a pH meter by adding drops of hydrochloric acid (BDH).

Equipment

Peristaltic pump Ismatec to pump the reagent and withdraw the organic layer; Rechargeable Micro mixerer, pH - meter WTW - SERLES Germany, to determine the required pH and atomic absorption device SHIMADZU - 6300, used to measure the proportion of copper (II) remaining in the organic layer.

extraction using droplet technique procedure

This method involves pumping a solution of dithizone at a concentration of (0.0001 mol) by a peristaltic pump[3], through a fine rubber tube connected to a fine needle to generate droplets for both the organic and aqueous phases at a rate of (1 drop/15-20 seconds) [4], after fixing the pump speed at (0.5 ml/200 seconds) for a certain volume to a certain volume of $CuCl_2$

after fixing the optimum conditions to complete the extraction process, which are: temperature (25-27 °C), pH = 1, and the speed of the micro mixer is the maximum. [5]

3. RESULT AND DISCUSSION

Design of a droplet premix extraction system

A new micro extraction system was designed using droplet premixing technology. It is a microsystem for generating aqueous and organic micro droplets and mixing them simultaneously through the surface tension of the droplets, followed by the use of a micro mixer that completes the extraction process by means of diffusion. This system enables the extraction process to be repeated several times in a short time, and the stages of the extraction process can be easily monitored while being worked on. The system working design consists of the following main components Figure 1:

1. Two micro needles for the aqueous and organic phases. Each micro needle is securely fixed by a movable magnetic clamp on a (1-30) cm graduated holder
2. Peristaltic pump device, to transfer the reagent and sample through the micro-rubber tubes to the two micro-needles
3. A micro blender that operates at different speeds (slow, medium, and high) and is .connected to a rechargeable battery
4. A 20 ml beaker in which the micromixer is used and the extraction process is completed.

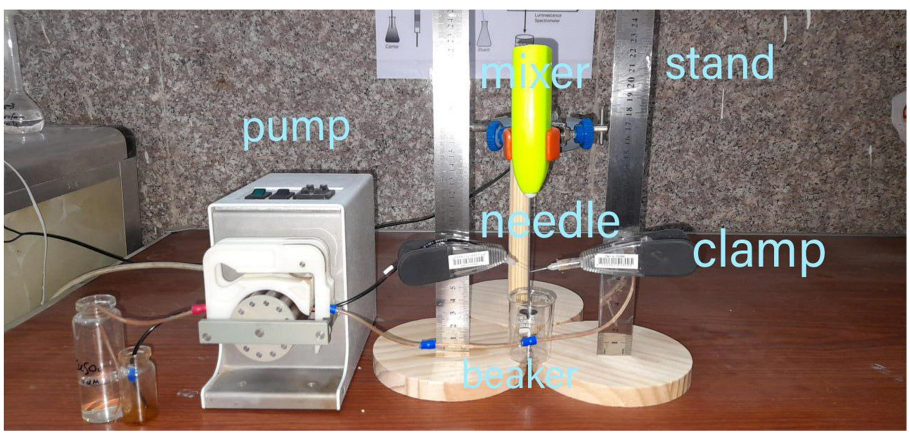

Figure 1. droplet extraction system design

Stages of the droplet extraction process

This new micro technology depends on the generation of regular and precise micro droplets for both the organic phase of the reagent (Dithizone) and the aqueous phase of the metal ion, $CuCl_2$. The speed of droplet formation can be controlled by regulating the speed of the micro pump. The micro extraction process (complexity) takes place by pumping a specific volume of the two solutions through The micro pump is made using microscopic rubber tubes. At the end of each tube is connected a fine micro needle through which water and organic droplets are generated. The micro extraction process with this technology goes through two stages:

The first: forming tiny micro-droplets and mixing them instantaneously during their formation, thus achieving (pre-mixing of the drops) so that the first micro-needle is perpendicular to the second, which allows the aqueous drop to mix during its formation with the organic drop and in reverse. This increases the surface area of micro-extraction and becomes the cornerstone of extraction.

Second: Using the micro mixer: After the pre-mixed drop descends, it will fall on the surface of the micro mixer, which in turn spreads the drop into very small particles in the form of a floating circular halo of a dark red color (which indicates that the extraction process has been achieved) on the inner wall of the baker or the vessel in which it is being conducted. It involves the extraction process, which greatly increases the surface area, so that every new droplet descending will spread over the aura referred to, and thus the process of mixing and spreading is repeated, which enhances the efficiency of extraction. The efficiency of this new method of extraction with drops results from precise control over the generation of droplets and their mixing in the formation phase, then Enhancing the extraction and repeating it after each new drop falls on the surface of the mixer, and after the process is completed and two layers are formed, the organic layer can be withdrawn in reverse or through a suitable pipette, after which the remaining copper in the aqueous layer is measured using a flame atomic absorption device. Shown from left to right are the stages of the extraction process using the droplet premixing technique Figure 2.

Figure 2. Stages of the droplet pre-mix extraction process

The effect of the main variables study

In this work, three main variables were studied to determine the extent of their impact on the extraction rate that occurs using the droplet technique[6], [7] as follows:

The effect of the concentration of $CuCl_2$ on the extraction process

Thermodynamic equilibrium and kinetics of extraction processes show that the metal ion concentration has a direct effect on the formation process of the extracted compound, which is important in obtaining the best values of the distribution constant D and the degree of extraction %E. Therefore, the copper(II) extraction process was performed by taking two volumes of copper chloride 2 (5 ml) each, the first concentration is (0.001 M) and the second concentration is (0.0001 M), at pH = 1 and after pumping (5 ml) From the dithizone solution at a concentration of (0.001 M) each at a pumping speed (0.5 ml/200 sec), with the maximum speed of the mixer, the organic layer is drawn from the aqueous layer by the pump. [8], [9]. The percentage of copper remaining in the aqueous layer is measured in both samples. After calculating the D and %E values, it was found that the second concentration (0.0001M) is better for the droplet technique extraction process, because it gives higher values than the first concentration (0.001M), as shown in Table 1. [10]

Table 1. The optimum copper (II) concentration for the bubbles extraction process.

sample NO.	Copper(II) concentration	D	E%
1	0.001M	13.8	79
2	0.0001M	15	97

The effect of changing the speed of the micropump on the extraction efficiency

The change in the speed of the peristaltic pump was studied into four speeds (ml/10 s), (ml/20 s), (ml/30 s), and (ml/40 s). (Figure 3) shows that the extraction degree value %E rises slightly with increasing pump speed between (ml/20s and ml/30s), after which the %E values decrease with increasing pump speed rate; The reason is that the formation and mixing of drops requires a special mechanism, So that each water droplet mixes with an organic droplet to form a single mixed droplet and descends vertically onto the surface of the mixer at a rate of several seconds for each descending droplet. This system requires the pump speed to be moderate in order to mix well, and the high speed of the pump does not allow The extraction process is suitable and efficient. Therefore a flow rate of (0.2ml/30 s) was chosen.

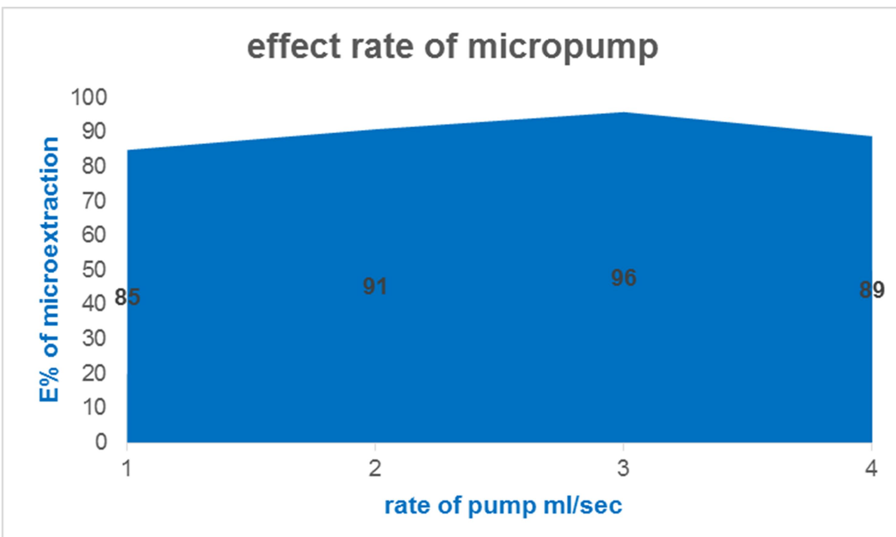

Figure 3.Effect of pump speed on microextraction.

Study the effect of equal volumes:

In this study, four volumes of dithizone solution (1, 2, 3, 4 ml) were injected into the specified copper (II) chloride solution in the same volume, respectively, for each stage of the extraction process during the study. When the pump speed is at (0.2ml/30 sec), and the micromixer speed is maximum. Figure 4 shows the results of the study as follows: The results of the study showed that equivalent volumes of both the organic reagent solution and the aqueous metal ion solution give high extraction rates, as this allows a high extraction process, so that each water droplet can mix with the organic droplet in equal proportions of volumes. Thus, equal volumes are suitable for this technique for precise extraction with one drop. However, when the sizes differ, this will reduce the extraction efficiency and will not allow the droplets to be mixed properly, nor will a balance be achieved for the extraction process The mechanism of this method depends on equal sizes

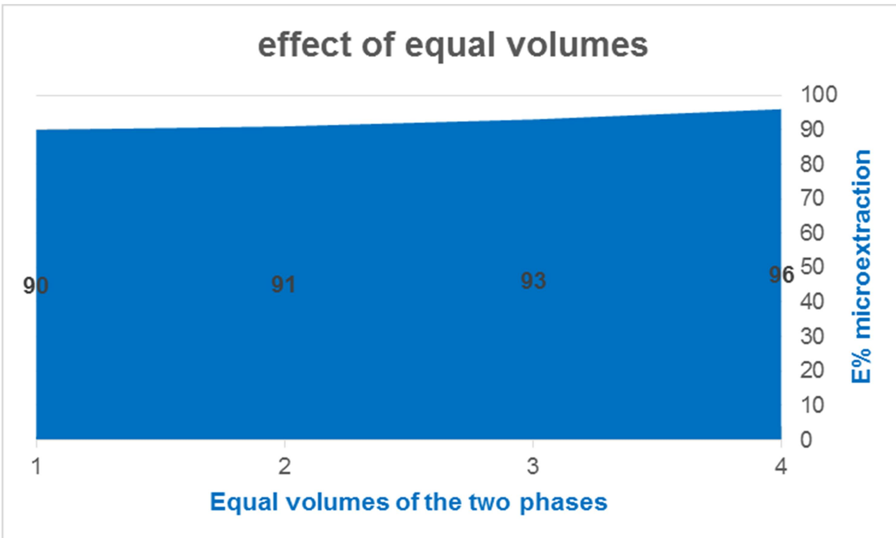

Figure 4. Effect of equal volumes on microextraction

Study the effect of micromixer speed on extraction efficiency

In this study, equal volumes of CuCl2 solution and dithizone solution were pumped, and the effect of different speeds of the micromixer (slow, medium, high) on the degree of extraction was studied, with the pump speed fixed at 0.2 ml/40 seconds. (Figure 5) showed that the values of %E increase with increasing speed of the micromixer until the maximum speed is reached, which represents the best result, which gives a larger surface area for extraction due to the fact that the droplets coming down from the microneedle upon contact with the surface of the mixer will spread greatly into a number of small particles on the surface. The surface of the inner container and this process is repeated after each falling drop, leading to the appearance of a (swimming circular halo) consisting of the mixing of microscopic parts of the aqueous and organic layers until extraction is complete (as this can be seen through the design of the technology as previously mentioned). The maximum speed is considered the most appropriate for extraction because the degree of extraction is satisfactory

and the slower speed of the mixer leads to the formation of larger particles and thus the extraction efficiency decreases.

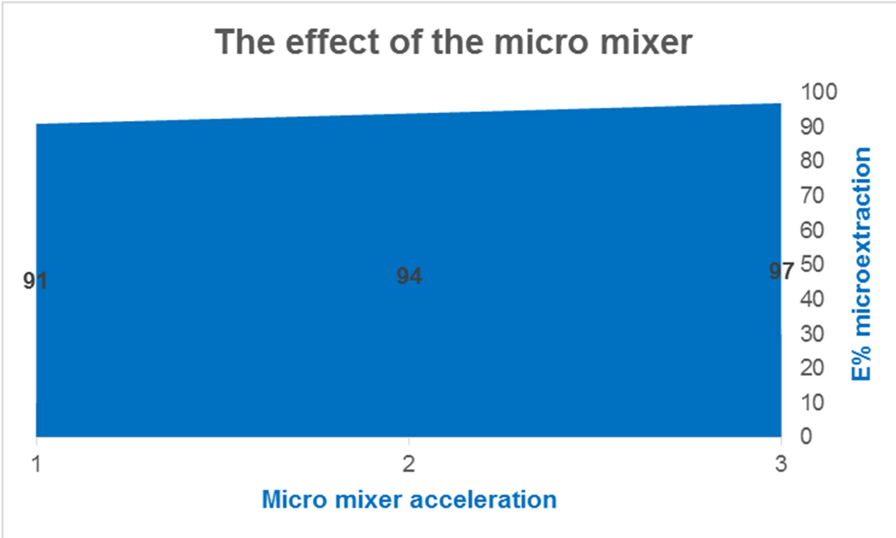

Figure 5 Study the effect of micromixer speed

4. CONCLUSIONS

A new microfluidic extraction method has been designed using droplet premixing technology[11], using simple tools and an efficient design[12], suitable for chemical and biological analyzes with high accuracy, as the microextraction efficiency reaches 97% and has advantages that achieve the principles of green chemistry[13]. The design adopted in this way generates microdroplets of solvent which are mixed during their formation phase and the extraction is enhanced using a small mixer that repeats the extraction process with each descending mixed droplet. [14]

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