



## New laboratory method extraction using ultrasound device by microbubble vortex phenomenon

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### ABSTRACT

Innovative, sensitive and accurate method for liquid-liquid extraction using an ultrasonic device is presented in this work. A working system was created, consisting of two basic components: the ultrasonic device and the pump device, to pump or withdraw the organic layer. A study of the key variables derived from the liquid-liquid system was carried out in the system containing Dithizone ( $1 \times 10^{-3}$  M) in (Chloroform)  $\text{CHCl}_3$  solvent. and aqueous copper (II) chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ) ( $1 \times 10^{-6}$  M) solution to determine the degree to which they affect the extraction performance attained in this manner. The effect of initial sample copper concentration and ultrasonic time, temperature effect, pump speed, were studied, establishing the best conditions for a sample of (10 mL) aqueous solution of Cu (II) chloride, the optimum copper (II) concentration in the analyzed sample is ( $1 \times 10^{-6}$  M), the ultrasonic time for the device is (8 min), and the flowrate of the pump is (3mL/30sec) and a temperature ( $27^\circ\text{C}$ ) and ( $\text{pH}=1$ ). The extraction degree was optimum under these conditions ( $96 \pm 2\%$ ). The innovative ultrasonic extraction method's results were compared to previous studies, and they were found to be more efficient than the traditional methods of extraction using funnel separation and multiple extraction.

**Keywords:** *ultrasonic device, Peristaltic pump, dithizone solution copper (II) chloride*

### INTRODUCTION

Water is essential for both human survival and the survival of all living organisms. Water consumption has increased in recent years as the global population has increased [1]. Meanwhile, residential and industrial agriculture generate significant amounts of wastewater containing hazardous and lethal contaminants such as suspended solids, pathogens, nutrients, and heavy metals [2]. Many pollution concerns will arise if they are not treated and safely discharged back into the sea or rivers [3]. Heavy metals are one of the contaminants discovered in wastewater [4]. Anthropogenic sources of heavy

metals in wastewater include electronics assembly and production, textiles, fertilizer and pesticide use, and mining operations [5] [6]. Even in low concentrations, these heavy metals can be harmful to species, including humans [7]. Traditional techniques for removing heavy metal ions from wastewaters include ultra-filtration, reverse osmosis, ion exchange, solvent extraction, sedimentation, and chemical precipitation [7]. However, many of these methods have shortcomings, such as insufficient metal removal [6]. To maintain environmental and human well-being, we must develop new techniques for the inexpensive removal of trace

pollutants from water while consuming minimal energy [8][9]. In this study, a novel technique was put forth to facilitate accurate and efficient extraction with high extraction rates.

### **Experimental**

#### **Chemicals**

Every chemical used in this study was provided by businesses (Fluka & BDH). At a concentration of (0.001M), dithizone solution (C<sub>13</sub>H<sub>12</sub>N<sub>4</sub>S) (Fluka) was created by dissolving (0.0256g) in (10 mL) of CHCl<sub>3</sub> (BDH). In order to meet the needs of the study, a different group of Dithizone solutions with a concentration of (0.001M) were created by mixing (5mL) of the previous Dithizone solution of (0.01M) with (50mL) of CHCl<sub>3</sub> in a standard volume vial, then storing the mixture in an opaque bottle away from light [10] [11]. An aqueous solution of copper (II) chloride (CuCl<sub>2</sub>.2H<sub>2</sub>O) (Fluka) at a concentration of (0.01M) was prepared by dissolving (0.42625mg) in a small volume of distilled water, then completing the volume to (250 mL) in a standard volumetric vial and saving the solution for use. Another group of CuCl<sub>2</sub>.2H<sub>2</sub>O solutions with a concentration (0.000001M) was prepared for the study's requirements by taking (0.5 mL) of the previous copper (II) chloride solution of (0.01M) and diluting it in (50mL) of distilled water in a standard volumetric vial, when the concentration is Copper (II) standard (0.06356 ppm). The acidity of the **CuCl<sub>2</sub>.2H<sub>2</sub>O** solution is adjusted to pH=1, and the pH is measured using a pH meter after a small amount of HCl is added (BDH).

#### **Equipment**

Glassware, volumetric flasks, and beakers were washed and rinsed with acetone and heated (150 °C), Ultrasonic device(AUSTRIA), thermometer, Peristaltic pump to pump the reagent and withdraw the organic layer; pH - meter WTW –SERLES Germany, to determine the required pH and Atomic Absorption Spectroscopy device SHIMADZU - 6300, used to measure the proportion of copper (II) remaining in the aqueous layer.

#### **Ultrasonic device extraction working procedure**

(10 ml) of an aqueous copper chloride solution (CuCl<sub>2</sub>.2H<sub>2</sub>O) at a concentration of (1 ×10<sup>-6</sup> M) was pumped into a volumetric vial containing (10 ml) Dithazone solution at a concentration of (0.001 M). By a peristaltic pump, through a rubber tube, after fixing the pump speed at (3 ml/30 sec) and after determining the optimal conditions for completing the extraction process which are: temperature (27 °C), pH = 1, and an ultrasonic device that generates vortices and waves help in the extraction process and with a constant vibration time of (8 minutes), The ultrasonic waves create cavitation bubbles in the solution, which generate localized high pressures and temperatures upon collapse. This promotes the breakdown of copper-containing minerals and facilitates the release of copper ions into the solution.

## **RESULT AND DISCUSSION**

#### **Ultrasonic extraction system design**

A new working system was designed using ultrasound technology, which is a device for generating eddy currents and waves that aid in the extraction process. This system allows the extraction process to be repeated several times in a short time, and it is easy to follow the stages of the:

- A device that generates vortices and waves that help in extraction, an ultrasonic device, which is the main part of the design, which has different timings (90 seconds - 8 minutes)
- The peristaltic pump device, which allows the reagent material to be transferred back and forth from the analyzed sample.
- A thermometer for measuring the temperature that has been stabilized at (27 °C).
- A round flask with a single-hole lid, for pumping organic matter.

Figure (1).



**FIGURE 1:** Ultrasound extraction

***The effect of the main variables study***

In this work, four main variables were studied to find out their impact on the percentage of extraction that occurs using the ultrasound device compared to other traditional methods, as follows:

***1-The effect of the concentration of CuCl<sub>2</sub>.2H<sub>2</sub>O on the extraction process***

The concentration of the metal ion has a direct influence on the formation process of the extracted compound [12], which is important in obtaining the best values for the distribution constant D and the degree of extraction %E. Therefore, the extraction of copper (II) was

carried out by taking two volumes of CuCl<sub>2</sub>.2H<sub>2</sub>O (10 ml) per of them, the concentration of the first (1 x 10<sup>-4</sup> M) and the concentration of the second (1 x 10<sup>-6</sup> m), and after pumping (10 mL) of a dithizone solution at a concentration of (1 x 10<sup>-3</sup> M), with a with time(6 min) for the device, the organic layer was withdrawn from the aqueous layer by the pump. The percentage of copper remaining in the aqueous layer is measured in both samples. After calculating the values of D and %E, it was found that the second concentration (1 x 10<sup>-6</sup> M) is better for the ultrasonic extraction process, because it gives higher values than the first concentration (1 x 10<sup>-4</sup>M), as shown in the table 1.

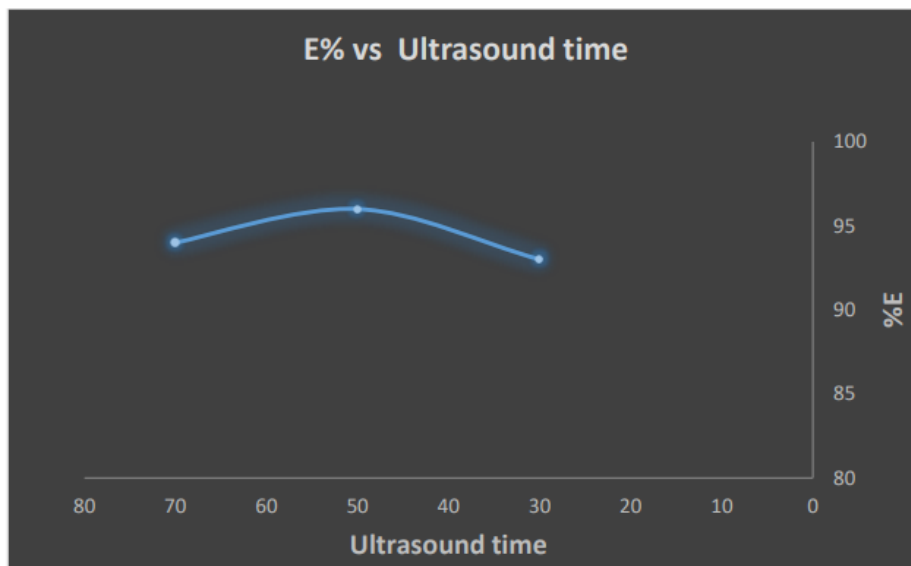
**TABLE 1:** Optimal copper (II) concentration for the ultrasonic extraction process

sample NO.	Copper(II) concentration	D	E%
1	1×10 <sup>-4</sup> M	3.7	89
2	1×10 <sup>-6</sup> M	14	92

***Study the effect of change the Ultrasound time***

In this study, four times equal volumes (10 mL) of CuCl<sub>2</sub>.2H<sub>2</sub>O solution and dithizone solution were steadily pumped with varying Ultrasound time for each (3 min), (8 min), and (13 min) for extraction process. pump speed (4mL /30sec), at a temperature of 25 . (Fig. 1) shows that the values of %E increase with increasing vibration

time, allowing more time for waves to pass through and complete the extraction. We believe that (8 minutes) is the best extraction time, Where the extraction rate in the time of (8 minutes) was approximately %E (94.5%) because the extraction degree is satisfactory and longer time means more energy consumption. Figure 1.

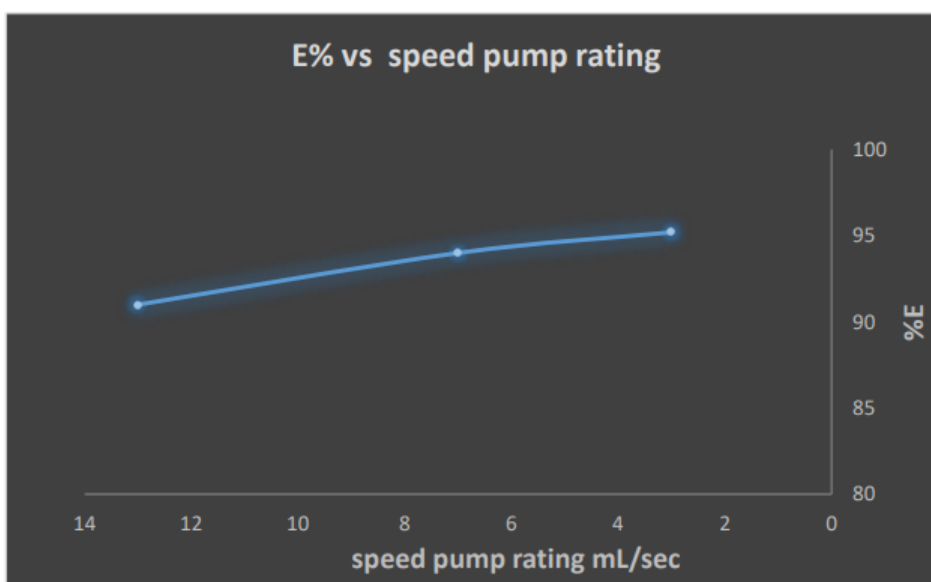


**FIGURE 1:** The effect of change the Ultrasound time

***Effect of changing in the rate of pump speed***

The change in pump velocity to three speeds (3mL/30sec), (5mL/30sec), and (7mL/30sec) was studied and ultrasonic time(8min). (Fig. 2) shows that the value of the degree of extraction %E rises slightly as the pump speed increases between (3mL/30sec and 5mL/30sec), after that the values of %E decreases as the rate of pump speed increases. The reason is due to the low flow rate of the pump the mechanical energy generated by ultrasound is applied further to the samples to

speed up extraction. This technique relies on the application of high frequency sounds and a limited amount of solvent to produce an efficient extraction of the compounds. On the contrary, the high speed of the pump does not allow the ultrasonic extraction process to be completed to sequentially increase the organic layer of peristalsis. Where the results show that the best speed of the pump is (3mL/30sec), the values of %E (95.3%).



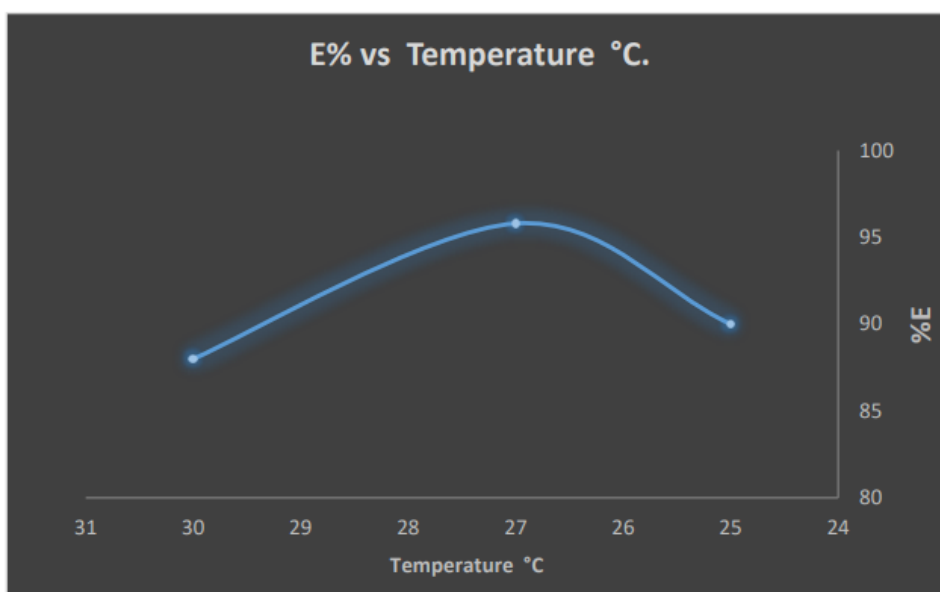
**FIGURE 2:** Effect of change the rate of pump speed

**Studying the effect of temperature**

An equal volume of copper(II) chloride solution (10 ml) and dithizone solution (10 ml) were studied at different temperatures (25 °C, 27 °C, 30 °C) under optimal conditions of vibration time of the ultrasonic device (8 minutes), and speed of the peristaltic pump (3 ml/30 seconds). The

results showed that The percentage of extraction decreases with increasing temperature at (30°C) as it negatively affects the extraction process as a result of evaporation of the solvent, so the best temperature for extraction is at 27°C (17). Table 4. Shows the results of the study.

Temperature °C	E%
25 °C	90%
27°C	95.8%
30°C	88%



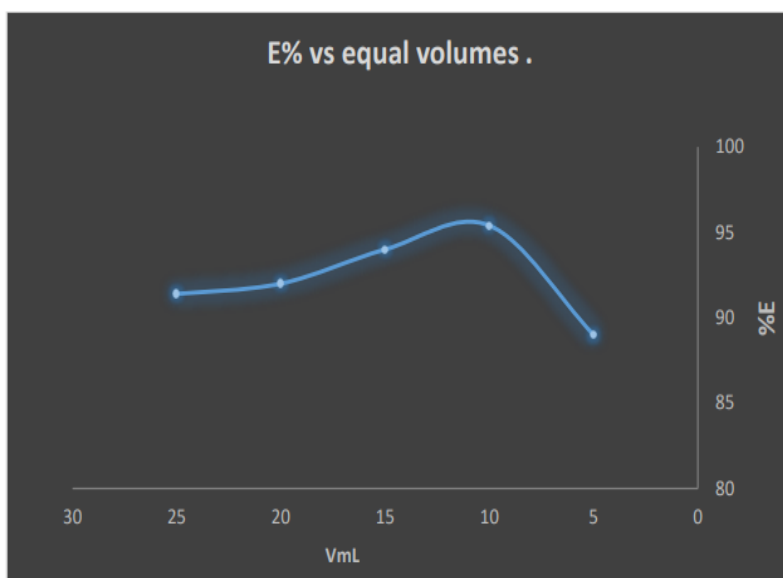
**FIGURE 5:** Studying the effect of temperature

**Study the effect of equal volumes**

During the extraction process, volumes of copper(II) chloride solution were injected (10, 15, 20, 25 mL) in dithizone solution respectively in the same volume for each stage of the study. When the pump speed is(3mL/30sec), the Ultrasound time is (8 minutes), and the temperature is (27 °C). The results of the study were as follows: The results of the study showed

that the constant volume (10 ml) between the two solutions gives a higher result for the values of E% and the distribution coefficient D than the total volume (20ml) between the two solutions. Help generate stable waves within the remaining space of the bottle, giving better scope for the extraction process, the values of E% (95.4%). As shown in the figure 3. Table 2

sample NO.	Volume	E%
1	5 ml	89%
2	10ml	95.4%
3	15ml	94%
4	20ml	92%
5	25ml	91.4%



**FIGURE 3:** Study the effect of equal volumes

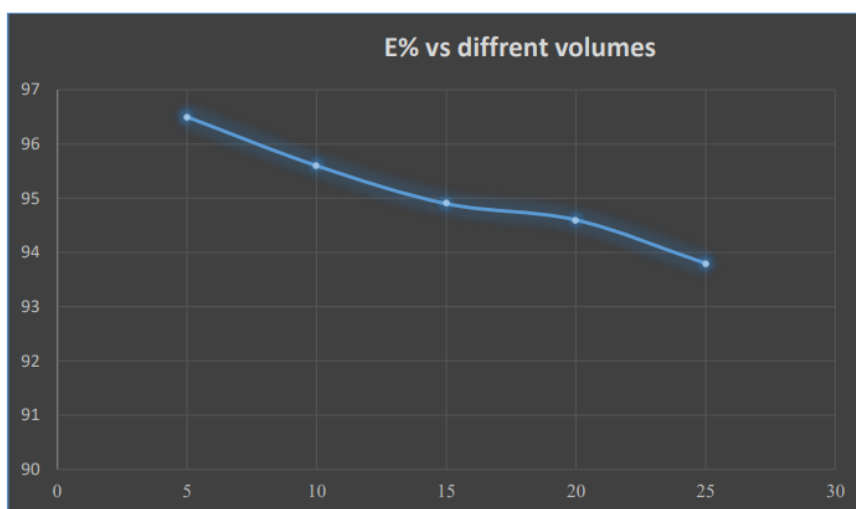
**Studying the effect of different volumes**

In this study, five different volumes of copper (II) chloride solution (5,10, 15, 20 ,and25 mL) were sequentially injected into a fixed volume of dithizone solution (10 mL) for each stage of the

extraction process, when the pump speed was set to (3mL/30sec) and the Ultrasound time was set to (8 min) and the temperature is (27 °C), the values of E% For the two volumes (5mL -10 mL) for both solutions is (96.5%)

**TABLE 3:** Shows the results of the study.

sample NO.	Volume of dithizone	Volume of Copper	E%
1	10ml	5ml	96.5%
2	10ml	10ml	95.4%
3	10ml	15ml	93.1%
4	10ml	20ml	91%
5	10ml	25ml	90%



**FIGURE 4:** Studying the effect of different volumes



**Accuracy of the ultrasound extraction method**

An analyzing samples was made from a substance called copper solution with a concentration of (0.06356ppm), and it was analyzed by both methods. This ultrasonic extraction technique was compared to the traditional approach described in [13], which

uses funnels division in the dithizone extraction procedure. Using the ideal conditions investigated for the ultrasonic extraction—pump speed (3mL/30sec), vibration time (8min), and temperature (25–30°C)—the extraction degree was higher ( $90 \pm 0.2$ ). Table shows the outcomes.

**TABLE 4:** Comparison of the results of ultrasonic extraction and the conventional method

Extraction method	Cu(II) concentration (ppm)	Dithizone concentration (M)	shake time (min)	D	E%
ultrasound extraction	1000	0.001[14]	8	10	90%
Traditional	1000	0.001	30	1.73	78.5

**CONCLUSIONS**

The conclusion from (Table 4) shows that the novel extraction technique using the ultrasound device is suitable for ease of use, speed of work, reduction of material and a solvent use, as well as the minimal environmental impact that enters it in the use of green chemistry. In contrast to multiple extraction, which requires additional time and physical effort when employing a separation funnel, ultrasound extraction is completed in a single step.

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