

Drop-drop Microextraction Enhanced by Two Opposite Surface Acoustic Waves

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Abstract

A droplet-droplet microextraction enhanced by two surface acoustic waves in opposite propagation directions is proposed. A 2x2 interdigital transducer array with 27.5MHz center frequency was fabricated on a 128° yx-LiNbO₃ piezoelectric substrate using micro-electric technology. Two surface acoustic waves in opposite propagation direction were generated when a RF signal was applied to diagonal interdigital transducers. The movement of extractive matter particles within microextraction solution was accelerated due to the radiation of the surface acoustic waves. Then, the mass transfer between two phases was enhanced. An ionic liquid and an organic dye (acid green-25) solution were used for extraction experiments. Results show that the extraction was greatly enhanced by two surface acoustic waves in opposite propagation directional, and almost finished within 160 seconds when the RF signal power was 27.8dBm. The stability of microextraction solution was also improved due to the two opposite surface acoustic waves.

Keywords: surface acoustic wave, diagonal interdigital transducer, microextraction, drop

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1. Introduction

Liquid-liquid extraction is one of sample pretreatment technology for biochemical analysis [1], which has been widely applied to detect trace analyte in sample solution [2-4]. However, there is some disadvantages, such as the use of large volumes of expensive organic solvent, long extraction time and low extraction level, can be seen in traditional liquid-liquid extraction technology. Most organic solvents for liquid-liquid extraction are harmful to health, so new liquid-liquid extraction technology should be invented to solve these problems. A single drop microextraction is a good liquid-liquid extraction method, which can solve these problems. The volume of organic solvents can be reduced to several microliters [5]. One application mode of the single drop microextraction method is direct immersing an organic solvent into sample solution, which was presented originally by MA Jeannot in 1997 [6]. In this mode of single drop microextraction procedures, the needle of microsyringe containing 1-3 microliters organic solvents is immersed into sample solution in a vial. The organic solvent drop is suspended from the needle tip by depressed a plunger on the vial. A stirring setup is used for reducing microextraction time and improving microextraction level. After equilibration, the drop is drawn back into the syringe and immediately subjected to analysis by an instrumental method. Due to these advantages, the single drop microextraction method is found application in assay of ethanol in alcohol-free cosmetics [7], determination of amitriptyline residues in waste water [8] and analysis of organochlorine and pyrethroid pesticides in tea samples [9]. However, the single drop microextraction is only applicable to liquid samples containing non-polar or moderately polar analyses, which limits its application in biochemical analysis. In addition, a stirring setup is usually used to improve microextraction speed and level, which will cause the instability of the solvent drop on tip of syringe.

Headspace single drop microextraction is another application mode of single drop microextraction. The method was presented in 2001 [10], and was rapidly developed. In this mode of single drop microextraction, a solvent drop on the tip of syringe was above the surface of sample solution with small gap. Analyze in sample solution was evaporated and dissolved into the solvent drop, and then, it was analyzed by instrument method. The main advantage of the headspace single drop microextraction is good stability of the solvent drop on tip of syringe

in spite of stirring sample solution. Together with gas chromatographic technique, the method has been applied to detect trace analyze in sample solution [11, 12]. However, it is almost only suitable for the consideration of volatile or semi-volatile analyses.

Single drop microextraction can reduce the volume of solvent to several microliters. However, the volume of sample solution is usually still several milliliters. To solve the problem of large volume of sample solution, drop-to-drop liquid-liquid microextraction is presented. In this drop-to-drop liquid-liquid microextraction mode, the volume of sample solution can be reduced to several microliters, while the solvent volume is several submicroliters. Pavithra [13] presented an electrowetting on dielectric (EWOD) drop-to-drop microextraction. An electric potential was applied between the top and a bottom electrodes with 1 kHz frequency to dispense and move donor and extractant drops, and then mixed and extracted each other. Drop-to-drop microextraction speed and level was accelerated by electrowetting forces.

Acoustic wave is not only applied in electric system [14, 15], but also in microfluidic systems. Surface acoustic wave (SAW) can be excited and transported along the surface of a piezoelectric substrate when an appropriate frequency electrical signal is applied to an interdigital transducer (IDT). As soon as the SAW meets with a drop on the piezoelectric substrate, the surface acoustic wave is radiated into the fluid, leading to internal acoustic streaming in the small fluid volume, which will accelerate the movement of particle or molecules in solution within the drop. This characteristic was used to enhance mass transfer in two phase drops, and then reduces the extraction time of drop-to-drop microextraction [16]. However, the SAW based drop-to-drop microextraction device has two disadvantages: (1) In order to prevent drop transportation along the substrate, hydrophilic area for accommodating drops should be formed on the hydrophobized substrate surface. The technology should be to be improved. (2) General speaking, the aperture size of the interdigital transducer is usually about 10~100 wave length, and the aperture size of one interdigital transducer is probably less than the size of sample solution, when the volume of the sample solution is large, such as dozens of micro-liters, for consideration of lowest detection limit of analyze.

Here, we present a new SAW based drop-to-drop liquid-liquid microextraction method to solve the problems above mentioned. 2×2 interdigital transducers array was fabricated on a $128^\circ\text{yx-LiNbO}_3$ piezoelectric substrate for exciting two surface acoustic waves in opposite propagation directions. Microextraction experiments of an organic dye (acid green-25) from aqueous solution to an iron liquid (1-butyl-3-methylimidazolium hexafluorophosphate) ([bmim][PF₆]) were also demonstrated to verify microextraction level and speed, which would be improved by two surface acoustic waves in opposite propagation directions.

2. Research Method

2.1. Experimental Setup

The experimental setup for the drop-to-drop microextraction enhanced by two surface acoustic waves in opposite propagation directions is shown as Figure 1.

In Figure 1, two pairs of interdigital transducers and reflectors are fabricated on the $128^\circ\text{yx-LiNbO}_3$ substrate using microelectric technology. Two diagonal interdigital transducers are connected to a power amplifier (TSA002A, TSH, China), which is used for amplifying a RF signal. The RF signal is generated by a RF signal generator (SP1461, EPRE, China). An aperture of every IDT is 4.32 mm, and a period is $\lambda=144\mu\text{m}$. The finger pair number of every interdigital transducer is 35. The areas free of electrode on the piezoelectric substrate are coated with Teflon AF 1600(USA, Dupont).

A highly sensitive CCD color video camera (DCE-2, Novel, China) is used to monitor the extraction process. MDVNT software (Novel, China) is used for camera control and image processing. A power meter (YM2462, Yamei, China) is used to measure the power applied to the diagonal interdigital transducers.

When a RF signal is applied to the diagonal interdigital transducers, two SAWs in opposite propagation direction are excited. As soon as the two SAWs meet with a drop, energies of two SAWs are radiated into the drop in an angle θ_R [17], which accelerate movement of analyte in the drop and then reduce extraction time and improve extraction level.

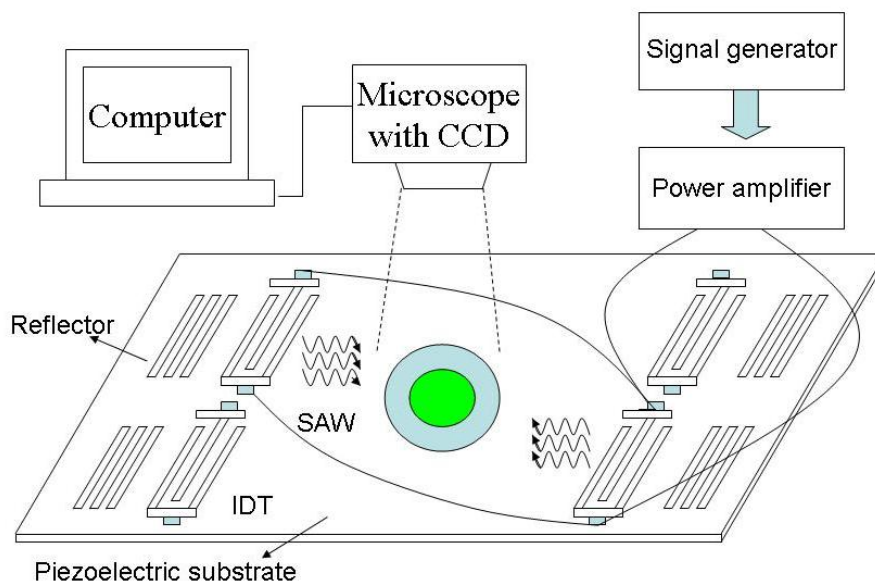


Figure 1. Experimental setup for drop-to-drop microextraction enhanced by two surface acoustic waves in opposite propagation directions

2.2. Chemicals and Materials

To verify the effect of drop-to-drop microextraction enhanced by two surface acoustic waves in opposite propagation direction, a microextraction experiment of an organic dye (acid green-25) from aqueous solution to an iron liquid (1-butyl-3-methylimidazolium hexafluorophosphate) ([bmim][PF₆]) has been designed and finished. The acid green-25 and [bmim][PF₆] are all bought from Suzhou Yacoo chemical reagent corporation in China. Purified water is used in experiments.

2.3. Drop-to-drop Microextraction Procedure and CIELab Color Model

First, sample solution and iron liquid droplets were pipetted on the surface of the piezoelectric substrate using a micro-syringe. Secondly, the diagonal interdigital transducers were applied a RF signal with 27.5MHz center frequency to generate two SAWs in opposite propagation direction, which would enhance mass transfer of acid gree-25 from aqueous phase to solvent phase, leading to reducing the extraction time. The extraction experiments were observed real time through the microscope with CCD, and stored in a person computer for further analyzing microextraction level.

Effect of RF signal power on microextraction level was analyzed by images based color model. Compared to RGB (red, green, blue) model and HIS (hue, saturation, illumination) model, CIELab (Commission Internationale de L'Eclairage defined lightness, and a, b colors) can response the color change of droplet more accurately, and insensitive to light intensity [18]. Thus, CIELab color model is used to measure the concentration of acid gree-25 aqueous solution for valuating microextraction level.

CIELab color model is a color pattern formulated by International Commission on Illumination in 1976, in which three parameters L, a, b are used to indicate a color intensity. As images pictured from CCD are RGB model, color spaces should be transformed from RGB to CIELab as following method [18].

First, RGB color space is transformed to XYZ color space by following formula:

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \frac{1}{255} \begin{pmatrix} 0.412453 & 0.357580 & 0.180423 \\ 0.212671 & 0.715160 & 0.072169 \\ 0.019334 & 0.119193 & 0.950227 \end{pmatrix} \cdot \begin{pmatrix} R \\ G \\ B \end{pmatrix} \quad (1)$$

Then, XYZ color space is transformed to CIELab color space:

$$\begin{aligned} L &= 116 \times f\left(\frac{Y}{Y_n}\right) - 16, \\ a &= 500 \times \left[f\left(\frac{X}{X_n}\right) - f\left(\frac{Y}{Y_n}\right) \right], \\ b &= 200 \times \left[f\left(\frac{Y}{Y_n}\right) - f\left(\frac{Z}{Z_n}\right) \right] \end{aligned} \quad (2)$$

Where the X_n, Y_n, Z_n are the XYZ values of a reference white point. The white point in color space is the standard D65 white point.

$$f(t) = \begin{cases} t^{\frac{1}{3}}, & t > \left(\frac{6}{29}\right)^3 \\ \frac{1}{3} \left(\frac{6}{29}\right)^2 t + \frac{4}{29}, & \text{others} \end{cases} \quad (3)$$

At last, CIELab color parameters can be calculated according to formula (1) to (3).

MATLAB software is used to select a region of interest from the image and to extract the averaged measurement over the region.

3. Results and Analysis

In order to observe the stability of drop in original position on the piezoelectric substrate, red dye solution drop was radiated by the two SAWs in opposite propagation direction. As a comparison, the same volume of red dye solution drop was also radiated by single SAW. Figure 2 shows the states of 9 μ l red dye solution drop acted by single SAW ((a) to (c)) and two SAWs in opposite propagation direction ((d) to (i)).

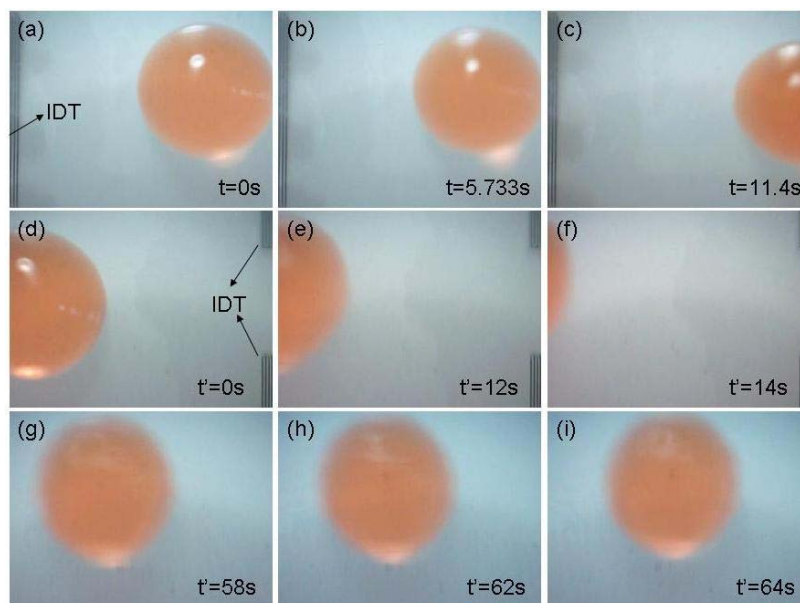


Figure 2. The sequential snapshots obtained from a recorded experiment for critical transportation of a drop. (a~c) 9 μ l red dye solution drop radiated by single SAW. (d~i) 9 μ l red dye solution drop radiated by two SAWs in opposite propagation direction.

In Figure 2, Figure 2 (a) shows the state of 9 μ l red dye solution drop on the acoustic path of single SAW. Figure 2 (b) to (c) show the slow movement of the drop actuated by single SAW, when RF signal power is increased to 24.9dBm. Figure 2 (d) shows the state of 9 μ l red dye solution drop in diagonal interdigital transducers. For observation, the drop is near one side of interdigital transducer array. Two SAWs in opposite propagation direction make the drop rotate along center of the drop, but cannot actuate the drop, when the RF signal power is less than 32.6dBm. As soon as the RF signal power increases to 32.6dBm, the drop is actuated slowly as shown in Figure 2 (e)-(f). However, the drop rotates along the center of drop when the drop is near the middle of diagonal interdigital transducers until 34.8dBm RF signal power as shown in Figure 2 (g)-(i). The main reason is as following: As the drop is near one side of interdigital transducer array at the beginning of critical transportation experimental, asymmetry of two surface acoustic waves on the drop occurs due to different length of acoustic transportation and acentric position. Therefore, 32.6dBm RF signal power can make the drop in the state of critical transportation. However, when the drop is near the center of two SAWs in opposite direction, internal acoustic streaming generated by the two SAWs is also near center symmetry, leading to rotation of the drop in original position at the 34.8dBm RF signal power.

In Figure 2, one can also deduce that drop will be actuated by single SAW at small RF signal power, while the drop acted by two opposite SAWs cannot arrive at the state of critical transportation at great RF signal power. Thus, hydrophilic area is usually indispensable in single SAW situation [16], which increases process sequence of microextraction device.

In addition, aperture width in diagonal interdigital transducers array can be at least double in single interdigital transducers. It is important when sample solution is easy to be obtained, and analyte concentration is very small, where the sample volume is probably dozens of microliters due to low detection limit.

Microextraction enhanced by two opposite SAWs was also demonstrated using homemade microextraction device. An organic dye (acid green-25) was extracted from aqueous solution drop to an iron liquid (1-butyl-3-methylimidazolium hexafluorophosphate) ([bmim][PF₆]) drop on the piezoelectric substrate. Figure 3 shows the sequential snapshots obtained from a recorded drop-to-drop microextraction experiment enhanced by two SAWs in opposite propagation direction.

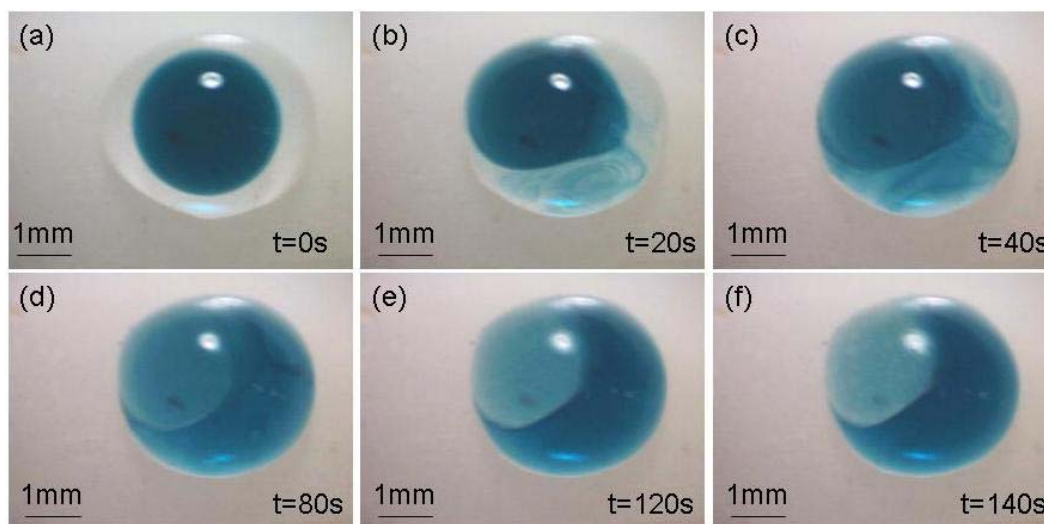


Figure 3. The sequential snapshots obtained from a recorded drop-to-drop microextraction enhanced by two SAWs in opposite propagation direction

In Figure 3, Figure 3 (a) shows the state of 5 μ l iron liquid and 4 μ l acid green-25 aqueous solution drop on the piezoelectric substrate. Figure 3 (b) shows the state of acid green-25 rotating within the drop acted by two opposite SAWs at 27.8dBm RF signal power. Figure 3 (c) to (f) shows the mass transfer of acid green-25 from aqueous phase to iron liquid phase.

Color change of aqueous phase and iron liquid can be observed intuitively, which shows the mass transfer of acid green-25 within two phases.

In order to calculate the parameter 'a' of CIELab to evaluate the microextraction level, the boundary of acid green-25 aqueous solution should be fit with polygon at first. Figure 4 shows the boundary and fit curve of acid green-25 aqueous solution shown in Figure 3 (a).

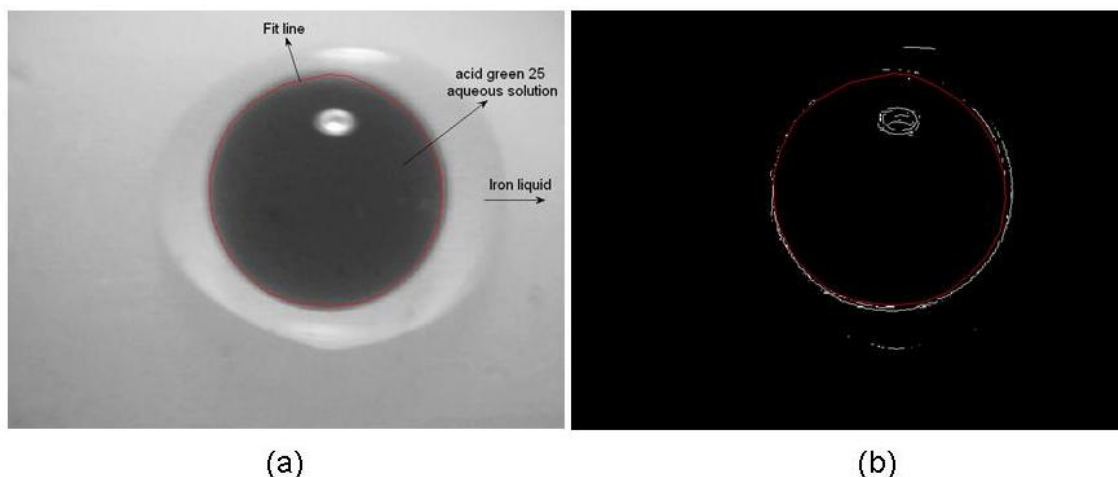


Figure 4. Grey-scale map of acid green-25 extraction solution (a), and its boundary (white line), fit curve (red line) (b)

Figure 4 shows that the fit curve is near the boundary of acid green-25 aqueous solution, and can be used for calculating parameters of CIELab model.

As the concentration of acid green-25 aqueous solution is corresponding to the parameter 'a' value of CIELab model [16], we can obtain the concentration of acid green-25 aqueous solution real time only when we calculated the 'a' value of CIELab model according to recorded images. In addition, it is important to study the effect of RF signal power on microextraction level. Figure 5 shows the concentration of acid green-25 aqueous solution drop with microextraction time at three different RF signal power. For intuition, column diagram is used in Figure 5.

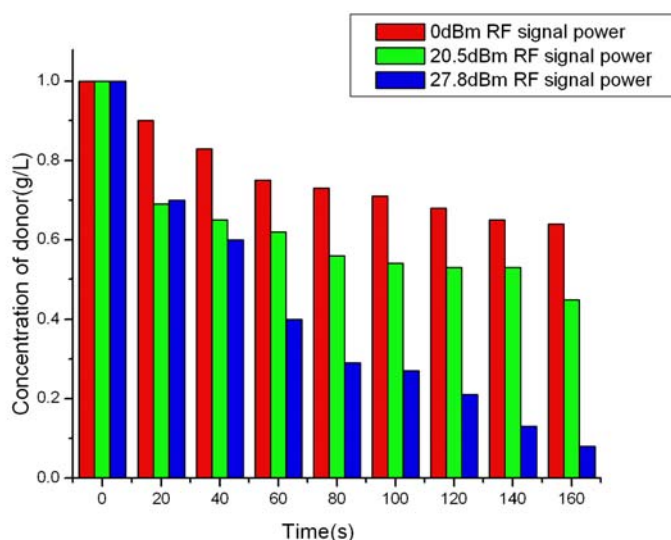


Figure 5. The concentration of acid green-25 aqueous solution drop (donor) with microextraction time at three different RF signal power

According to the microextraction results as shown in Figure 5, one can deduce that two SAWs in opposite propagation direction can accelerate microextraction speed and level, and is affected greatly by RF signal power applied to the diagonal interdigital transducers. When RF signal power is 27.8dBm, the concentration of acid green-25 aqueous solution can be reduced from 1g/L to about 0.1g/L within 160 seconds microextraction time. After microextraction, analyte can be further analyzed by instrument method such as gas chromatograph technology.

4. Conclusion

A new drop-to-drop liquid-liquid microextraction method was presented, in which microextraction was enhanced by two SAWs in opposite propagation direction. Microextraction of acid green-25 from aqueous solution to iron liquid was demonstrated to verify validity of the method. According to the microextraction experiments, several conclusions can be drawn: (1) Drop-to-drop microextraction can be accelerated by two SAWs in opposite propagation direction; (2) Simulating to single interdigital transducer situation, RF signal power applied to diagonal interdigital transducers will also greatly affect the drop-to-drop microextraction speed and level; (3) Compared to single SAW situation, there exist advantages of simpler technology and flexible volume of sample solution in two SAWs with opposite propagation direction situation. The presented microextraction method is valuable for piezoelectric microfluidic device for microfluidic analysis.

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