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# Thread-based microfluidic three channels device in combination with thermal lens detection for determination of copper and zinc

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## Abstract

A new method involving a thread-based microfluidic three channels device in combination with thermal lens detection is developed for the sequentially determination of Cu (II) and Zn (II) in this paper. The thread-based microfluidic three channels device was composed of a U-shaped supporter and thread-based microfluidic three channels fixed on the supporter. The different types of threads (cotton and cotton-polyester threads) in the thread-based microfluidic three channels device were used as the efficient transporting channels of the sample, reagent and buffer solutions, driven by capillary and gravity actions. The fabrication and determination conditions were investigated. By utilizing the differences of the transporting rates of the thread-based microfluidic three channels and combining with the thermal lens detection, the Cu (II) and Zn (II) were sequentially determined at the different pH in a complex system. The results show that TLS is an excellent detection method for the thread-based microfluidic analytical devices and can be widely applied to determination of other analytes.

**Keywords:** Thread-based microfluidic devices, Thermal lens, Zincon, determination of copper and zinc

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## 1. Introduction

The development of thread-based microfluidic analytical devices ( $\mu$  TADs) has been substantially increased in recent years.<sup>1-7</sup> Threads (Cotton, cotton-polyester and silk thread) have been employed for fabricating the  $\mu$  TADs due to their unique advantages, including the flexibility, light-weight, low-cost and easy to use, especially power-free liquid transport via capillary action. The use of thread as a liquid transporting channel for the fabrication of low-cost microfluidic diagnostics and biomedical assays was first reported by the groups of Shen and Whitesides, respectively.<sup>1, 2</sup> Since then, more  $\mu$  TADs have been use to detect protein, glucose, metal ions, immunoassay and chemical synthesis.<sup>3-7</sup>

Current detecting methods of  $\mu$  TADs rely on colorimetric measurement using a digital camera or scanner. However, this method cannot accurately measure the change of color of  $\mu$  TADs. A problem is that a color measured by electronic devices of different models may not be identical. The errors are generated in the colorimetric measurement because of the differences in hue, lightness and saturation. It reduces the reliability of colorimetric result interpretation: different users of the same device may obtain different interpretations of the same colors.<sup>6</sup> To develop a high-sensitivity detection method is probably one of the most important encountered problem for the development of  $\mu$  TADs.

Laser thermal lens spectrometry (TLS) is a high sensitive spectrometry based on photothermal effect.<sup>8</sup> The effect is a result of the heat generated in an irradiated sample by non-radiative relaxation of absorbed energy. When a laser beam with Gaussian profile passes through an absorbing sample, the absorption of the laser beam by the analytes produces temperature gradient in sample. This temperature gradient leads to a corresponding change of refractive index of the solution, forming the thermal lens. The intensity of thermal lens is measured by its effect on the divergence of the same laser beam (single TLS) or of the divergence of another probe laser beam (dual laser TLS). TLS offers high sensitivity (up to  $10^{-8}$  mol/L),<sup>9</sup> good spatial resolution, and is suitable for the detection of the micro-volume sample and easy to be combined with the hyphenation method and preconcentration procedures.<sup>10-12</sup>

Zn (II) and Cu (II) are essential for normal physiological processes of living organisms. These two elements are always together in nature. Due to Zn (II) and Cu (II) have important role in

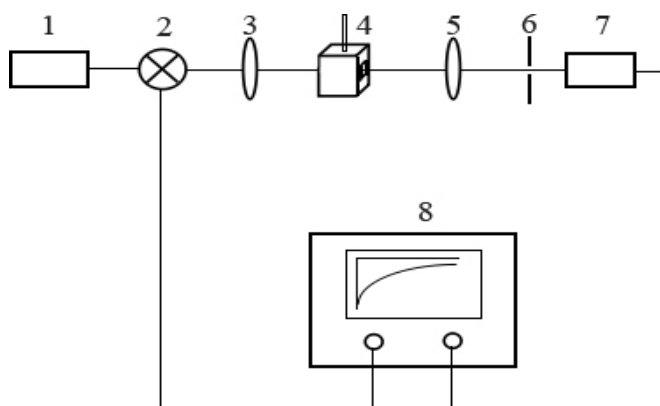
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3 biological, industrial, and medical science, therefore, it is important to measure trace amount of Zn  
4 (II) and Cu (II) in the presence of each other.<sup>13-16</sup>

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7 In this work, a method for the determination of copper and zinc ions is developed by  
8 combining a thread-based microfluidic three channels device with thermal lens detection. The  
9 fabrication and determination conditions were optimized. Two types of threads (cotton and  
10 cotton-polyester threads) were utilized as the efficient liquid transporting channels in the  
11 thread-based microfluidic three channels device. The micro-volume sample obtained by the  
12 thread-based microfluidic three channels device. The micro-volume sample obtained by the  
13 thread-based microfluidic three channels device was analyzed by TLS, and the content of Zn (II)  
14 and Cu (II) was sequentially determined in a complex system. The results show that the TLS is an  
15 appropriate method for the detecting micro-volume sample obtained by the  $\mu$ TADs.  
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## 23 2. Experimental

### 24 2.1 Apparatus and materials

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29 Near-field laser thermal lens spectrometer used in this experiment has been described in detail  
30 elsewhere (Fig.1).<sup>17, 18</sup> A He-Ne laser ( $\lambda_{632.8\text{nm}}$ , TEM<sub>00</sub>) acts as both exciting and probing beam.  
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32 The measurement power of the laser is 12 mw, and the power at the sample location is 10 mw.  
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34 After being modulated and focused, the laser beam irradiates on a detection micro-cell located at  
35 the confocal distance. The micro-cell has a 5 mm pathlength and an 8.0  $\mu$ L volume. In order to  
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55 **Fig. 1** Schematic diagram of near-field laser thermal lens spectrometer (1, laser; 2, chopper; 3, lens;

56 4, micro-cell; 5, expanding lens; 6, pinhole; 7, detector; 8, lock-in amplifier and computer

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achieve the detection of TLS in near field from the radiation source, the laser beam passed through the micro-cell is expanded by an expanding lens. The TLS signals produced in the determination solution are detected and processed by a pinhole/photoelectric device and a M5210 lock-in amplifier (EG&G, Princeton applied research, USA) and translates to a computer by ADC-DAC.

The intensity of laser beam passing through the micro-cell was measured during the thermal lens effect at initial time ( $I_{(0)}$ ), and steady-state time ( $I_{(\infty)}$ ). The magnitude of the thermal lens signal and the sensitivity of the techniques depend on the absorbance of the sample and thermo-optical properties of the sample (such as  $dn/dt$ , the temperature coefficient of the refractive index and  $K$ , thermal conductivity of the medium) as given by Eq.(1):

$$S_{\text{TLS}} = \frac{I_{(0)} - I_{(\infty)}}{I_{(\infty)}} = - \frac{2.303(dn/dt)}{\lambda K} PA$$
$$= 2.303EPA \quad (1)$$

$$E = - (dn/dt) / \lambda K \quad (2)$$

where  $E$  represent the so-called enhancement factor compared to conventional transmission measurements,  $A$  is absorbance of sample,  $P$  is the excitation laser power and  $\lambda$  is the laser wavelength.<sup>8,9</sup>

Spectra measurements were made using a UV-2550 UV-Vis spectrophotometer (Shimadzu, Japan). The atomic absorption spectrophotometer (AAS) was used for comparing the determination results. Measurement of pH was performed by using a PHS-25C precision pH/mV meter with a combined glass electrode (Shanghai Lida instrument factory, China).

Natural cotton, cotton-polyester and silk threads (The threads have a average diameters of 0.22 ± 0.02mm, white) were obtained from the local market (Xi'an, China) and further treated by hydrophilic treatment in the current experiment.

## 2.2 Reagents and solutions

Zincon was purchased from Beijing Chemical Factory (Beijing, China). Copper nitrate and Zinc nitrate were obtained from Tianjin Ruijin Chemicals Co. Ltd (Tianjing, China). Borax was

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3 purchased from Xi'an Chemical Reagent Factory (Xi'an, China). Sodium acetate and sodium  
4 dodecylbenzenesulfonate (SDS) were purchased from purchased from Tanjing Bodi Chemical Co.  
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7 Ltd (Tianjing, China). Methanol, ethanol and acetone were obtained from Amresco (VWR,  
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9 Shanghai, China).

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12 5.0mmol/L zincon solution was prepared by dissolving 0.2312g of the zincon in 0.02mol/L  
13 NaOH solution. The stock solution was stored at 4°C (at least) for 1 week. Working zincon  
14 solution was prepared by diluting the reagent solution above in 0.02mol/L NaOH solution.  
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19 Metal stock solution of Zn (II) and Cu (II) were respectively prepared by dissolving the  
20 appropriate amount of metal nitrate in 100 ml of water and standardizing with EDTA. Then,  
21 working metal stock solutions were obtained from these solutions by further dilution with water.  
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26 A 0.2mol/L sodium acetate buffer for copper determination was prepared by dissolution of  
27 corresponding quantity of soil and the final pH was adjusted with acetate acid to 5.5. A 0.25  
28 mol/L borate buffer for zinc and copper determination was prepared by dissolution of  
29 corresponding quantity of soil in a solution containing 0.05mol/L potassium chloride and 0.5  
30 mol/L NaOH with the final pH adjusted with sodium hydroxide to 9.0.<sup>19</sup>  
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37 A mixed solution of Cu (II) and Zn (II): 5 mL working metal stock solutions of copper and  
38 zinc were respectively taken and mixed, then diluted to 50 mL with water.  
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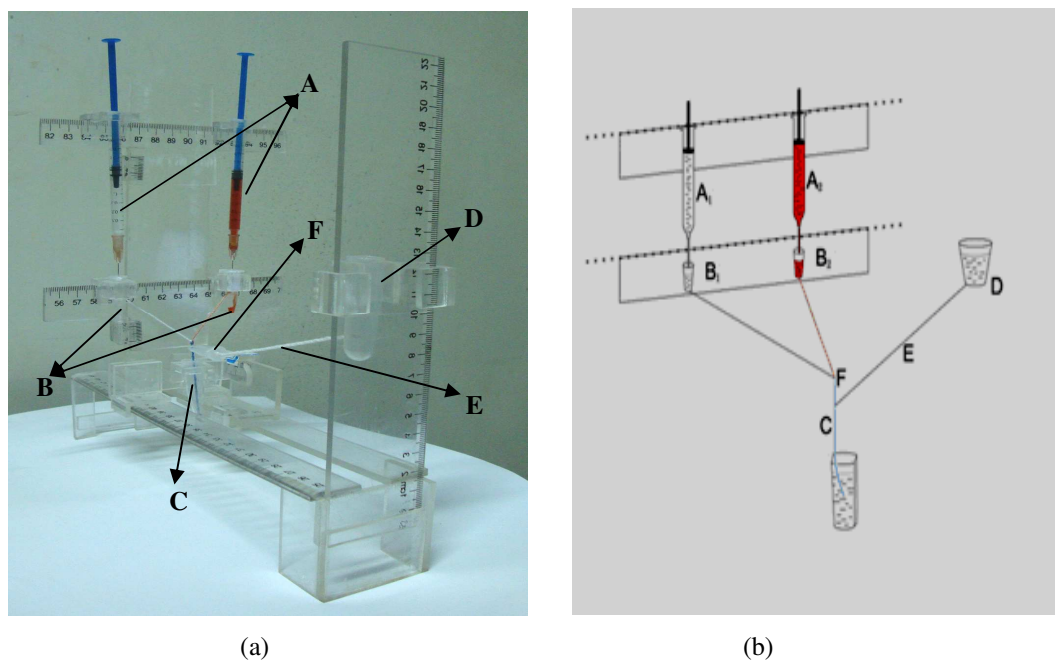
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42 All of chemicals used in the current experiment were of analytical-reagent grade. Double  
43 distilled de-ionized water was used throughout the whole process.  
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### 46 **2.3 Pretreatment of threads**

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48 In order to enhance the wicking property of the threads and remove any deposited wax, pectin or  
49 other hydrophobic contaminants on the threads, the threads (natural cotton and cotton-polyester  
50 threads) were conducted by hydrophilic pretreatment in a mixed solution of 1.5% NaOH and 3.0%  
51 SDS at 80°C for 30 min. Then, the threads were taken out and repeatedly washed with water to  
52 neutral. Finally, the threads were dried at room temperature.  
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## 2.4 Fabrication of thread-based microfluidic three channels device

The thread-based microfluidic three channels device used in the current experiment is shown in Fig.2. It was composed of a U-shaped supporter and thread-based microfluidic three channels fixed on the supporter. The U-shaped supporter was made of the polymer sheets bonded together. The thread-based microfluidic three channels were obtained by twisting together “Y” geometrics and



**Fig. 2** Photograph (a) and illustration (b) of thread-based microfluidic three channels device (A, micropipette; B, sample and reagent reservoirs; C, overall channel ; D, buffer solution reservoir; E, buffer solution channel; F, linked place of “Y-geometry” and buffer solution channels).

buffer solution channels, which fabricated with two types of threads, one being made of cotton-polyester and the other of cotton. The “Y” geometrics and buffer solution channels were respectively fabricated by braiding together four cotton-polyester and three cotton threads, and have a length of 12 cm and 4 cm and average diameters of  $0.86 \pm 0.02\text{mm}$  and  $0.63 \pm 0.02\text{mm}$ , respectively (The relatively large uncertainties in the measured channels diameter resulted from the non-uniform tightness of the braids.). Then, the “Y” geometrics and buffer solution channels were respectively assembled on the U-shaped supporter at a certain inclination angles ( $\tan\theta$ ). A scale printed on the U-shaped supporter provided a convenient measure of the inclination angle ( $\tan\theta$ ) of the microfluidic three channels assembled on the supporter. Thus, the thread-based

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3 microfluidic three channels device was performed in the current experiment. In order to reduce the  
4 evaporation loss of solutions in the determination process, the thread-based microfluidic three  
5 channels device was integrally assembled in a plastic box.  
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9 As illustrated, there were three reservoirs on the U-shaped supporter as the determined sample,  
10 analytical reagent and buffer solution reservoirs (B and D), respectively. Two micropipettes (A) on  
11 the vertical arm of the U-shaped supporter were used to add the determined sample and analytical  
12 reagent solution into the sample and reagent reservoirs (B). The both ends of inlets of the “Y”  
13 geometrics channel were respectively immersed into the two reservoirs (B) filled with sample and  
14 analytical reagent solutions, and the end of outlet of the “Y” geometrics channel was placed into  
15 the detection micro-cell. The end of outlet of the buffer solution channel (E) was twisted together  
16 the “Y” geometrics channel, positioned at linked place (F) of the “Y” geometrics channel, and the  
17 end of inlet of the buffer solution channel was immersed into the buffer solution reservoir (D) so  
18 that the buffer solutions wicking along the channels could be mixed with the solution on the “Y”  
19 geometrics channel. Hence, these solutions were respectively introduced along each thread  
20 channels, driven by capillary and gravity actions. Since the liquids were transported faster through  
21 “Y” geometrics channel compared to the buffer solution channel at a certain inclination angle  
22 ( $\tan\theta$ ), the Cu-zincon complex was first formed and determined at pH 5.5. Then, the reaction  
23 acidity was changed when the borate buffer solution wicked along the buffer solution channel into  
24 the “Y” geometrics channel. The Cu-zincon and Zn-zincon complex were determined at pH 9.0.  
25 As the result, copper and zinc ions can be sequentially determined at the different pH in a complex  
26 system.  
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29 In addition, the inclination angle ( $\tan\theta$ ) of the “Y” geometrics and buffer solution channels  
30 assembled on the U-shaped supporter can be respectively adjusted in order to control the  
31 transporting rate and change reaction acidity in the current experiment.  
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## 34 2.5 Experimental procedures

35 First, 500 $\mu$ L of the mixed solution of Cu (II) and Zn (II) (or determined sample) and 500  $\mu$ L of  
36 35 $\mu$ mol/L zincon were respectively applied to the sample and reagent reservoirs on the U-shaped  
37 supporter using two micropipettes. Then, 600 $\mu$ L of 0.2 mol/L sodium acetate buffer (pH 5.5) was  
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added to the buffer solution reservoir. These solutions were respectively introduced and mixed along each thread channels, driven by action of capillary and gravity. Cu (II) in the mixed solution firstly reacts with zincon to form the Cu-zincon complexes (pH 5.5) at 12 min. Subsequently, the buffer solution was replaced with another reservoir filled with 600 $\mu$ L of 0.25 mol/L borate buffer (pH 9.0). After 5 min, the borate buffer solution introduced into the “Y” geometrics channel and changed the acidity of the complex reaction. Cu (II) and Zn (II) react with zincon, forming the complexes of Cu-zincon and Zn-zincon at pH 9.0. Thus, the content of Cu (II) and Zn (II) were sequentially determined by TLS without a pre-separation in the complex system based on the acidity difference of complex reaction.

### 3. Results and discussion

#### 3.1 Complexation characteristic and absorption spectra

Zincon, 2-carboxy-2'-hydroxy-5'-sulfoformazylbenzene, is a sensitive reagent for spectrophotometric determination of Cu (II) and Zn (II) in aqueous solution. It has shown that zincon is as a quadridentate ligand to coordinate zinc and copper ions with two oxygens (OH, COOH) and two nitrogens (N=N, NH) (Fig.3). Their values of the equilibrium constants for the Zn-zincon and Cu-zincon complex are high pH dependent. The pk values (formation constant of

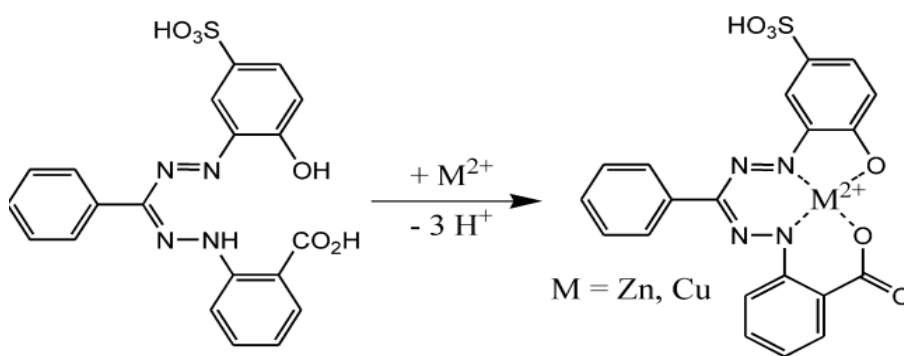
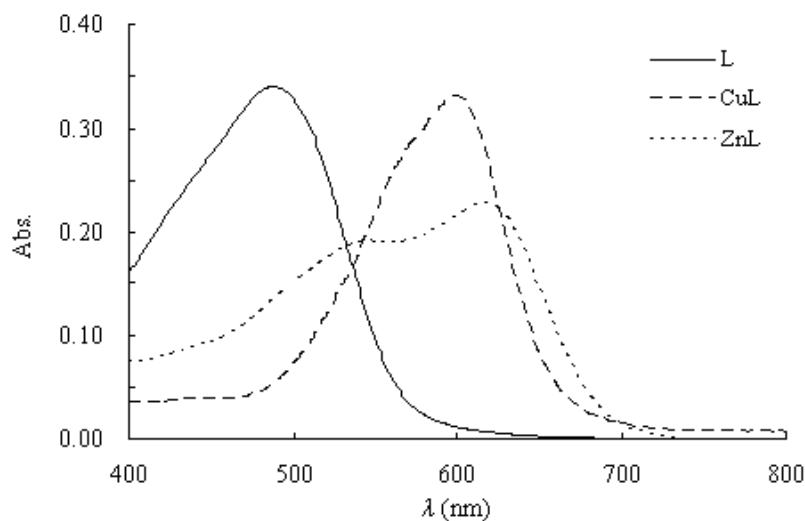


Fig. 3 Structures of zincon in its free and metal-bond forms

complex) for the Zn-zincon complex are respectively 7.9 and 0.6 at pH 9 and 5.5, showing that the complexation of Zn (II) at pH 5.5 is insignificant; whereas the formation of Cu-zincon complex is

favoured at pH 5.5.<sup>20</sup> The molar absorptivities of the complexes are  $1.9 \times 10^4$  for Cu-zincon at pH 5.0 to 9.5 and  $2.3 \times 10^4$  for Zn-zincon at pH 8.5 to 9.0, respectively. The characteristics of the complex reaction shows that Cu (II) and Zn (II) can be sequentially determined without a pre-separation in a complex system based on the acidity difference of complex reaction. Thus, Cu



**Fig. 4** Absorption spectra of zincon (L) and complex of Cu-zincon (CuL) and Zn-zincon (ZnL)

(II) was first determined at pH 5.5, and then changing the acidity, the total content of Cu (II) and Zn (II) were determined at pH 9.0 in the current experiment.

The absorption spectra of zincon (L) and the complexes of Cu-zincon (CuL) and Zn-zincon (ZnL) were respectively measured and shown in Fig.4. The results show that the absorption spectra of the complexes of Cu-Zincon and Zn-Zincon exhibit maximum absorption at 600 nm and 620 nm, respectively. It shows that maximum absorption wavelength of the complexes can be matched with the laser output wavelength of TLS ( $\lambda_{632.8 \text{ nm}}$ ) well, and the chromogenic reagent background is free.

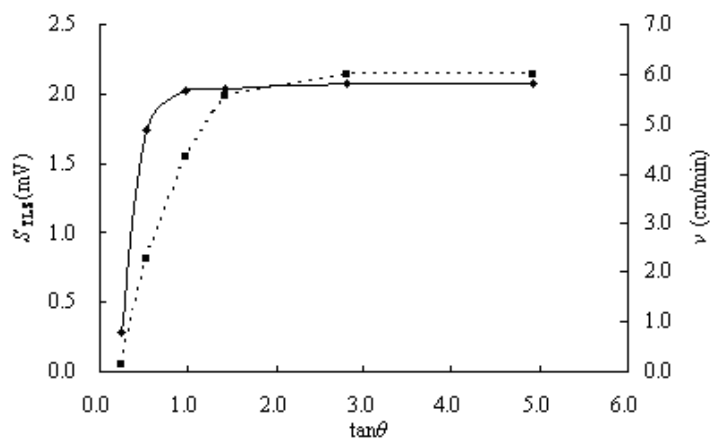
### 3.2 Selection of threads

It is very important to select the appropriate type of thread for the fabricating thread-based microfluidic three channels device. The material of thread determines the transporting rate of liquids along it, and is a crucial parameter in design of any  $\mu$ TADs because the liquid

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4 transporting rate is difference for the different types of threads. In order to achieve that Cu (II) and  
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6 Zn (II) can be sequentially determined without a pre-separation at different acidity in a complex  
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8 system, the liquid transporting rate was investigated for the different types of threads (natural  
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10 cotton, cotton-polyester and silk threads). A 10  $\mu$  L of dye solution was used to investigate the  
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12 transporting rate through these threads. In comparison with the natural cotton, cotton-polyester  
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14 and silk threads, there was a significant difference in the liquid transporting rate. The liquid  
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16 transporting rate of cotton-polyester thread was faster than that of the natural cotton thread, and  
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18 the slower in liquid transporting rate was silk thread. The liquids transporting rate depends on the  
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20 small gaps between the constituent fibers of the threads.<sup>3,5</sup> It is possible that the cotton-polyester  
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22 thread is composed of different materials of fibers (cotton and polyester fibers) and have the larger  
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24 gaps between the constituent fibers. Since liquids are transported faster through braided or twisted  
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26 thread channels compared to the single ones,<sup>5</sup> the four cotton-polyester and three cotton threads  
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28 braided together were selected as the “Y” geometrics and buffer solution channels, respectively.

### 29 30 **3.3 Effect of inclination angle**

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32 As was mentioned above, the transporting rate is related to the inclination angle ( $\tan\theta$ ) of the  
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34 thread-based microfluidic three channels fixed on the U-shaped supporter. The inclination angle of  
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36 the thread-based microfluidic three channels not only can adjust the transporting rate of the  
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38 determined sample, analytical reagent and buffer solution but also change the conditions of  
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40 complex reaction. The effect of inclination angle of the “Y” geometrics and buffer solution  
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42 channels fixed on the U-shaped supporter on the determination was respectively tested by using a  
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44 dye solution as the model sample in the experiment. Same results were obtained for the “Y”  
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46 geometrics and buffer solution channels and showed in Fig.5. The signal intensity of TLS and  
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48 transporting rate were found to be rapidly increased with the increasing of the inclination angles of  
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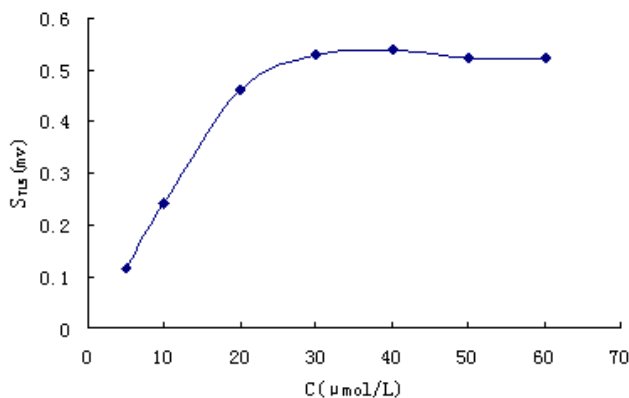


**Fig. 5** Effect of inclination angle of the “Y” geometrics and buffer channels (— signal intensity of TLS ; .....transporting rate)

each thread channels fixed on the U-shaped supporter. The signal intensity of TLS and transporting rate were basically stable when the inclination angle of the channels was greater than  $\tan\theta$  2.0. Therefore, the thread-based microfluidic three channels were fixed on the U-shaped supporter at inclination angles  $\tan\theta$  3.0 in the current experiment.

### 3.4 Effects of zincon concentration

The effect of zincon concentration on the determination of Cu (II) and Zn (II) was tested. The result was shown in Fig.6. As shown in Fig.6, the signal intensity of TLS increased as the zincon



**Fig. 6** Effect of zincon concentration

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3 concentration increased gradually, and then became constant when the concentration of zincon  
4 was higher than  $30 \mu\text{mol/L}$ . Thus,  $35 \mu\text{mol/L}$  of zincon was selected for the determination of Cu  
5 (II) and Zn (II) in the current experiment.  
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### 9 10 **3.5 Effect of organic solvents**

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12 It is known that the intensity of the TLS not only depends on the optical absorption of the  
13 determination analyte but also the thermo-optical properties of the solution medium. The use of  
14 binary mixtures of water and organic solvents can change the thermo-optical properties of the  
15 solution medium and enhance the detection sensitivity of TLS.<sup>17, 18, 21</sup> The selected solvent should  
16 have a high sensitivity enhancement, and the maximum absorption of the complex in the selected  
17 binary mixtures of water and organic solvents can match the wavelength of the exciting laser in  
18 TLS well. The effect of the binary mixtures of water and organic solvents on the determination of  
19 Cu (II) and Zn (II) was studied. The result shown that the common used solvents of methanol,  
20 ethanol and acetone could all meet the requirements mentioned above. A sensitivity enhancement  
21 of comparison was performed for methanol, ethanol and acetone. It was found that the  
22 enhancement of the binary mixtures of water-acetone was greater than that of water-methanol or  
23 ethanol because of the advantageous thermo-optical properties of acetone (The enhancement  
24 factors of acetone,  $E = - (dn/dt) / \lambda K$ , is 2360 for  $\lambda 632.8 \text{ nm}$ .<sup>22</sup>). By comparison with that of  
25 water medium, the TLS sensitivity of copper-zincon and zinc-zincon complexes was respectively  
26 increased about 60% and 48% by used the binary mixtures of water-acetone (1:2, V:V). Therefore,  
27 the binary mixtures of water-acetone (1:2, V:V) was selected as the solvents for the TLS  
28 determination of Cu (II) and Zn (II).  
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### 46 **3.6 Interference experiment**

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48 The interference of some ions was studied in detailed. For this study, different amounts of the ions  
49 species were added to a mixed solution of copper and zinc containing  $1 \mu\text{g/ml}$  of each. The  
50 tolerated limits were taken as those concentration causing changes no greater than  $\pm 5\%$  in the  
51 concentration of metal ions in the mixture. The results are summarized in Table 1. As is shown, the  
52 method is relatively specific for determination of Cu (II) and Zn (II).  
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**Table 1** Interferences of foreign ions on the determination of Cu (II) and Zn (II) ( $\mu\text{g/ml}$ )

Foreign ions	Tolerance limit	Foreign ions	Tolerance limit
Sr <sup>2+</sup>	500	K	1500
Hg <sup>2+</sup>	50	NO <sub>2</sub> <sup>-</sup>	1000
Bi <sup>2+</sup>	250	I <sup>-</sup>	1000
Cd <sup>2+</sup>	300	Na <sup>+</sup>	1500
Pb <sup>2+</sup>	200	SO <sub>4</sub> <sup>2-</sup>	1000
Mn <sup>2+</sup>	500	Ca <sup>2+</sup>	1000
Al <sup>3+</sup>	1000	CO <sub>3</sub> <sup>2-</sup>	1000
Co <sup>2+</sup>	60	CN <sup>-</sup>	1000
Fe <sup>3+</sup>	200	PO <sub>4</sub> <sup>3-</sup>	1000
Mg <sup>2+</sup>	1000	Cl <sup>-</sup>	1000
Cr <sup>3+</sup>	500	Br <sup>-</sup>	1000
Ni <sup>2+</sup>	80	SCN <sup>-</sup>	1000

### 3.7 Calibration curve and recovery

Under the optimized conditions, the calibration curve for determination of Cu (II) and Zn (II) was obtained by the proposed method. The determination result and recovery are respectively shown at Table 2 and Table 3. A good linear relationship was obtained over the range of 0.3~5.0

**Table 2** The results of determination of Cu (II) and Zn (II) ( $n = 3$ )

Analytes	Equation	Liner determination range ( $\mu\text{g/mL}$ )	correlation coefficient	LOD (S/N=3) ( $\mu\text{g/mL}$ )	RSD(%)
Cu(II)	$S = 0.3511[\text{Cu}] + 1.4602$	0.3 ~ 5.0	0.9995	0.20	2.96%
Zn(II)	$S = 0.3010[\text{Zn}] + 0.9258$	0.3 ~ 7.0	0.9886	0.25	3.79%

$\mu\text{g/mL}$  for Cu (II) and 0.3~7.0  $\mu\text{g/mL}$  for Zn (II), respectively. The regression equations were  $S_{\text{Cu(II)}}$

= 0.3511[Cu] + 1.4602 and  $S_{Zn(II)} = 0.3010[Zn] + 0.9258$ . The linear correlation coefficients for determination of Cu (II) and Zn (II) were 0.9995 and 0.9886, respectively. The limit of detection (LOD,  $3\sigma/k$ ,  $n = 3$ ) was found to be 0.20 and 0.25  $\mu\text{g/mL}$  and the relative standard deviation (RSD%) was 2.96% and 3.79% for determination of Cu (II) and Zn (II), respectively. The recoveries (R%) were obtained from synthetic mixtures over the range of 94.0~106.3 for Cu (II) and 97.4~105.3 for Zn (II).

**Table 3** Recovery of Cu (II) and Zn (II) in synthetic binary mixtures (n=3)

Sample	Amount added ( $\mu\text{g/mL}$ )		Amount found ( $\mu\text{g/mL}$ )			
	Cu	Zn	Cu	R (%)	Zn	R (%)
1	9.00	24.00	8.46	94.0	24.49	102.0
2	11.00	30.00	10.37	94.3	31.59	105.3
3	11.00	33.00	11.53	104.8	32.14	97.4
4	11.00	35.00	11.69	106.3	36.14	103.3

### 3.8 Applications

Hair sample was washed with acetone and water to remove the surface contamination. Then 1.0 g of clean hair sample was accurately weighed and dry-ashed in furnace at 450°C. The residue was dissolved in nitric acid. The pH of solution was adjusted to about 5.5 or 9.0 with hydrochloric acid and sodium hydroxide and the solution was diluted to 50 ml with water.

Trace elements in hair samples can indicate the metabolism and nutrition of the body. Content of Cu (II) and Zn (II) in hair sample are significance to the living organisms' metabolism. The proposed method has been applied successfully to the determination of Cu (II) and Zn (II) in hair samples. The results are respectively shown in Table 4. Compared with the results of determination by AAS method, the results shown a good agreement with the results obtained by AAS method for the same samples.

**Table 4** The results of determination Cu (II) and Zn (II) in hair sample (n=3)

Sample	Proposed method ( $\mu\text{g/g}$ )		AAS method ( $\mu\text{g/g}$ )		Relative error (%)	
	Cu (II)	Zn (II)	Cu(II)	Zn (II)	Cu (II)	Zn(II)
1	8.82	22.97	8.94	23.32	1.3	1.5
2	11.15	29.71	11.26	30.48	0.97	2.5
3	10.51	32.75	10.69	33.14	1.7	1.2
4	11.07	36.37	11.20	35.76	1.2	1.7

#### 4. Conclusion

In this paper, the thread-based microfluidic three channels device combining with thermal lens detection was developed for the first time. By using the difference of transporting rate of two types of threads, copper and zinc ions were sequentially determined in a complex system based on the complex reaction of copper and zinc ions with zincon at the different pH. The study shows that the thread is an excellent substrate for transporting fluid flow without external power and can be utilized to fabricate the more functional  $\mu$  TADs for the detection of chemistry, biochemistry, environmental and biology samples.

In the experiment, the sample, reagent and buffer solutions were respectively introduced and mixed along thread-based microfluidic three channels, driven by capillary and gravity actions. The transporting rate of the solutions can be changed by adjusting the inclination angle ( $\tan\theta$ ) of these channels assembled on the U-shaped supporter. The method could be readily applied to the designing and fabricating of other  $\mu$  TADs.

The micro-volume sample obtained with thread-based microfluidic three channels device can be measured sensitively by the TLS. TLS offers high sensitivity (comparable to or even better than that of other detection method such as AAS and UV-Vis spectrophotometer), and is a suitable determination method for micro-volume sample. The results show that TLS is a favorable detection method for the  $\mu$  TADs, which is practical and valuable for its wide applications. The proposed method, thread-based microfluidic analytical device combination with TLS detection,



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3 provides not only a detection sensitivity level but also has the advantage that it can be applied for  
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5 a larger number of analytes.  
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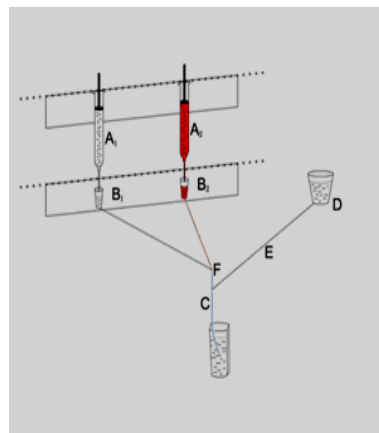
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## Thread-based microfluidic three channels device in combination with thermal lens detection for determination of copper and zinc

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A new method involving a thread-based microfluidic three channels device in combination with the thermal lens detection was developed for the sequentially determination of Cu (II) and Zn (II). The different types of threads were used as the efficient transporting channels of the sample, reagent and buffer solutions, driven by capillary and gravity actions. By utilizing the differences of the transporting rates of the thread-based microfluidic three channels and combining with the thermal lens detection, the Cu (II) and Zn (II) were sequentially determined at the different pH in a complex system.



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