

## Research Article

# Online Preconcentration and Determination of Trace Amounts of Zinc in Nature Waters

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A simple, sensitive, reliable and flexible flow injection spectrophotometric method is proposed for on-line preconcentration and determination of trace amounts of zinc in water. At the presence of Tween-80 in pH 9.3 buffer solutions, the shade of color of Zn (II)-PAN complex is in a linear relation to the zinc amount at the point of the maximum absorption peak of 560 nm. The optimal experimental conditions, including reaction conditions and preconcentration conditions, had been obtained. The linear range of the proposed method was between 2.0 and 360  $\mu\text{g L}^{-1}$  and the detection limit was 0.42  $\mu\text{g L}^{-1}$ . The relative standard deviation was 3.55% and 2.14% for 5.0  $\mu\text{g L}^{-1}$  and 50  $\mu\text{g L}^{-1}$  of zinc standard solution ( $n = 8$ ). The method had been successfully applied to zinc determination in water samples and the analytical results were satisfactory.

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## 1. INTRODUCTION

Zinc is an essential element in the nutrition of animals, human beings, and plants [1, 2]. Zinc plays an important role in replications, gene expressions, and the metabolism of nucleic acids and different proteins. However, zinc can be toxic when exposures exceed physiological needs. Zinc is present in food, soil, and water. Hence, determination of zinc (II) is indispensable. There are many methods for zinc determination such as spectrophotometry [3–5], atomic absorption spectrometry [6, 7], flame atomic absorption spectroscopy [8], graphite furnace atomic absorption spectrometry [9, 10], inductively coupled plasma atomic emission spectroscopy [11], and inductively coupled plasma mass spectrometry [12]. The above methods mentioned are of high sensitivity and accuracy. But some are expensive, some are time-consuming, some are troublesome, and others are toxic. Modern environmental monitor calls for automatic, safe, and simple analytical methods.

Preconcentration technique [13–16] can improve the detection limit as well as the selectivity of the method. Flow injection analysis (FIA) [17–19] can improve analytical procedures such as high analytical throughput, precision, accuracy, low reagents, and sample consumption. Therefore, a

new method was proposed for online preconcentration and spectrophotometric determination of low-concentration Zn (II) in water. The proposed method is based on the fact that Zn reacts with PAN to produce Zn (II)-PAN complex formation in the pH 9.3 buffer solution. To avoid the extraction procedure, it has been found that the PAN reacts with zinc to form a water-soluble complex at the presence of Tween-80.

## 2. EXPERIMENT

### 2.1. Apparatus

A model ZJ-la automatic metallic element analyzer developed and produced successfully by Professor Xinshen Zhang of our own laboratory was used. The analyzer has the functions of flow injection analysis (FIA), ion chromatography, and automatic sample injection. The function of automatic reference FIA was applied to determine Zn (II). Two analytical pumps (Shanghai Huxi Analytical Instrument Plant, Shanghai, China) of FIA were used to deliver solutions. One was used to deliver elution solution and reagent solution while the other delivered sample solution. Polytetrafluoroethylene (PTFE) tubing of 0.5 mm in internal diameter was used as the channels for all solutions to circulate.

Ultraviolet and visible spectra were obtained using a Spectrumlab S54 (Lengguang Technology Co., Ltd, Shanghai, China). The absorbance intensity was recorded at 560 nm on an IBM-PC. Data acquisition and processing were performed with HW-2000 chromatography software (Qianpu software Co., Ltd, Shanghai, China) running under Windows XP.

## 2.2. Reagents

All reagents used including 1-(2-pyridineazo)-2-naphthol (PAN) (Tianjin Ruijinte Chemical Reagent Plant, Tianjin, China), Tween-80, sodium tetraborate, o-phenanthroline, DDTC, and sodium hexametaphosphate (Chengdu Fang Zhou Chemical Reagent Plant, Chengdu, China), oxalic acid dihydrate, lithium hydroxide monohydrate, ammonium thiocyanate, and citric acid (Beijing Donghua Chemical Reagent Plant, Beijing, China) were of analytical grade and all solutions were prepared with deionized water.

## 2.3. Preparation of solution

Zinc stock solution: zinc stock standard solutions at a concentration of  $1000 \text{ mg L}^{-1}$  were obtained from China Environmental Monitoring Terminus, Beijing, China. Working solutions were prepared by suitable dilution of the stock solution.

Mixed chromogenic reagent solution (R): 10 mL of  $4 \times 10^{-3} \text{ mol L}^{-1}$  PAN ethanol solution, 20 mL of 8% Tween-80, 20 mL of pH 9.3 of sodium tetraborate buffer solution, 1.5 mL of 10% sodium hexametaphosphate, 1 mL of 0.1% DDTC, and 2 mL of o-phenanthroline were mixed and the mixture solution was diluted to 100 mL.

Elution solution: a total of 1.26 g of oxalic acid dihydrate, 1.576 g of citric acid monohydrate, and 1.15 g of lithium hydroxide monohydrate were dissolved in 1000 mL of water.

## 2.4. Preparation of preconcentration column

The preconcentration column developed by our laboratory was filled with macroporous spherical resin with 4-(2-pyridylazo) resorcinol (PAR) functional group. The PAR functional group can form chelate complex with determined metal ion in the preconcentration column and the chelate complex can be eluted by the eluent solution of oxalic acid-citric acid-lithium hydroxide. The filling granularity of resin was  $80\text{--}100 \mu\text{m}$ . The preconcentration column length was 40 mm and its internal diameter was 5 mm.

By filling the preconcentration column, mix resin and deionized water into pasty matter and drop slowly into column with burette. After sedimentating for a moment, resin was dropped slowly until the preconcentration column became full. Then, cover strainer, cover on the column, and wash a few minutes with deionized water for further work.

## 2.5. Analytical procedure

The FIA manifold used was outlined in Figure 1 with PTFE pipes. The sample solution was injected into preconcentra-

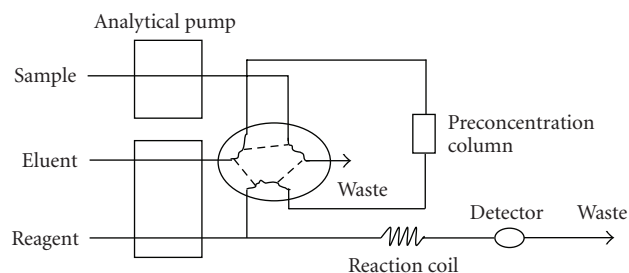


FIGURE 1: Schematic diagram of the flow injection concentration online.

tion column to preconcentrate with a six-way injection valve. When the instrument was put into analyzing position, the concentrated Zn (II) was eluted by eluent solution, pushed to the three-way cock, and mixed with chromogenic reagent solution in the reaction coil. The Zn (II)-PAN complex was then formed and carried into the flow cell. The absorbance intensity of Zn (II)-PAN complex was determined at 560 nm by detector and transformed to a signal of the peak which was recorded by HW-2000 software on a PC.

## 3. RESULTS AND DISCUSSION

### 3.1. Effect of reaction conditions

#### 3.1.1. Effect of pH

In the flow injection analysis, the absorbance of complex is affected by pH of the reaction medium. The effect of pH on the Zn (II)-PAN complex was tested in the pH range 4–11. The test results showed that the maximum peak height could be obtained when pH range was between 8 and 10. Thus, pH 9.3 of borate solution was selected as the buffer solution.

#### 3.1.2. Effect of PAN concentration

The reagent concentration was another important factor in flow injection analysis. The effect of PAN concentration on the peak height were tested from  $5 \times 10^{-5} \text{ mol L}^{-1}$  to  $1.2 \times 10^{-3} \text{ mol L}^{-1}$  in Figure 2. The results showed that the peak height rose when concentration of PAN changed from  $5 \times 10^{-5} \text{ mol L}^{-1}$  to  $4 \times 10^{-4} \text{ mol L}^{-1}$ , and the peak height declined when concentration of PAN changed from  $4 \times 10^{-4} \text{ mol L}^{-1}$  to  $1.2 \times 10^{-3} \text{ mol L}^{-1}$ . Therefore,  $4 \times 10^{-4} \text{ mol L}^{-1}$  PAN was selected for further work.

According to the reaction kinetics, the reaction rate will inevitably increase when increasing concentrations of the reagent. Thus, the absorbency will increase when increasing concentrations of PAN. However, the reaction rate will not increase when concentrations of the reagent reaches a certain value. Therefore, when PAN consumption reaches a certain value, the concentration of PAN which reacts with zinc should be certain because zinc concentration is fixed in the sample. Thereby, the absorbency will not increase when increasing PAN concentration. On the contrary, the background color (baseline noises) will increase because the free state PAN in the system will increase.

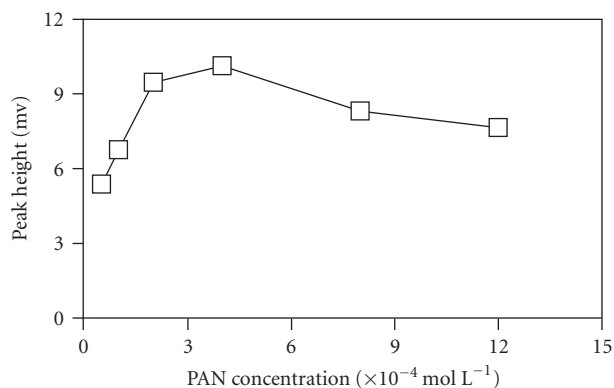


FIGURE 2: Effect of PAN concentration on the peak height.

### 3.1.3. Effect of Tween-80 concentration

The Zn (II)-PAN complex was hydrophobic. Thus, Tween-80 was selected as reagent which could increase solubility of the system. The test results in Figure 3 showed that the peak height increased when concentration of Tween-80 changed from 1.0% to 1.6% and that the peak height did not increase even when concentration of Tween-80 changed from 1.6% to 2.2%. Therefore, 1.6% Tween-80 was selected as the optimal concentration for the further work.

### 3.1.4. Effect of flow rate

In the FIA, the flow rate could affect the sensitivity of the proposed method. In the study, the flow rate was adjusted by the interior diameter of pump pipe. Therefore, the effect of the flow rate of reagent solution on the peak height was studied from 0.10 mL min $^{-1}$  to 0.72 mL min $^{-1}$ . The test results showed that the best flow rate could be obtained when the flow rate of reagent (R) was set at 0.23 mL min $^{-1}$ .

### 3.1.5. Effect of the reaction coil length

In the flow injection analysis, the reaction time is adjusted by the length of reaction coil. If reaction coil was too short, the reagents would react incompletely. If reaction coil was too long, it would be time-consuming. Therefore, reaction coil length from 1 to 5 m was tested. The study results in Figure 4 showed that 3 m of the reaction coil length was the optimum and further increase of reaction coil length did not increase peak height. Thus, 3 m of the reaction coil length was chosen as optimal parameter.

## 3.2. Effect of preconcentration conditions

### 3.2.1. Effect of filling granularity and length of preconcentration column

Length of preconcentration column and filling granularity could affect the effect of preconcentration. In the study, filling granularity of 80 ~ 100  $\mu$ m was selected and length of concentration column from 20 mm to 100 mm was tested. The results showed that the shorter the length of concentra-

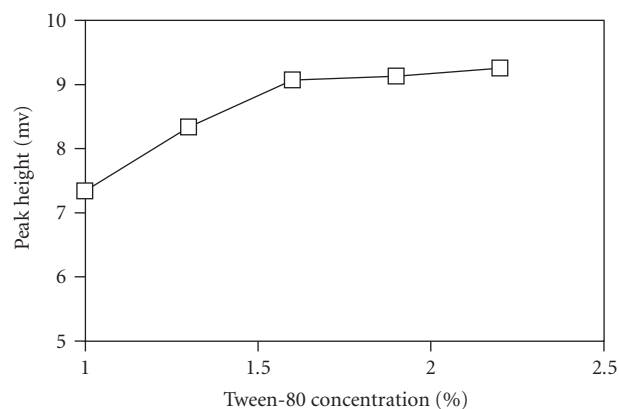


FIGURE 3: Effect of Tween-80 concentration on the peak height.

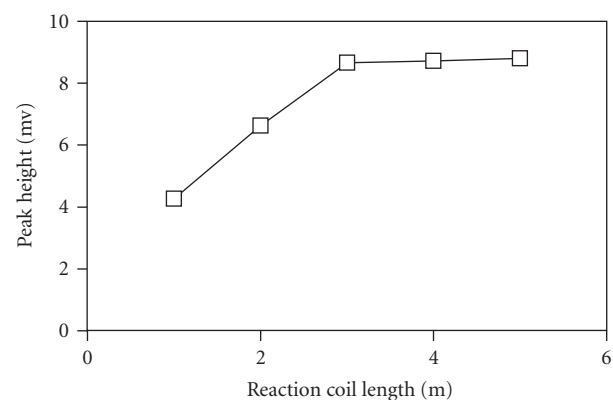


FIGURE 4: Effect of reaction coil length on the peak height.

tion column, the higher the sensitivity. However, if the length of concentration column was too short, the concentration of preconcentration Zn (II) in samples was not adequate, which lowered the sensitivity. The highest sensitivity was obtained when the length of concentration column was 40 mm. Thus, 40 mm of concentration column length was selected for further study.

### 3.2.2. Effect of preconcentration time

Preconcentration time can affect analysis sensitivity and sampling frequency. Preconcentration time from 2 minutes to 13 minutes was tested. The results in Figure 5 showed that the preconcentration time was longer, the zinc concentration of the preconcentration column would be higher which causes the analysis sensitivity to be higher but the sampling frequency to be lower. Taken a comprehensive consideration of analysis sensitivity and sampling frequency, preconcentration time of 5 minutes was decided for further work.

### 3.2.3. Effect of preconcentration rate

Either too high or too low preconcentration rate was not proper. Too high-preconcentration rate would increase analysis sensitivity but augment pressure of preconcentration

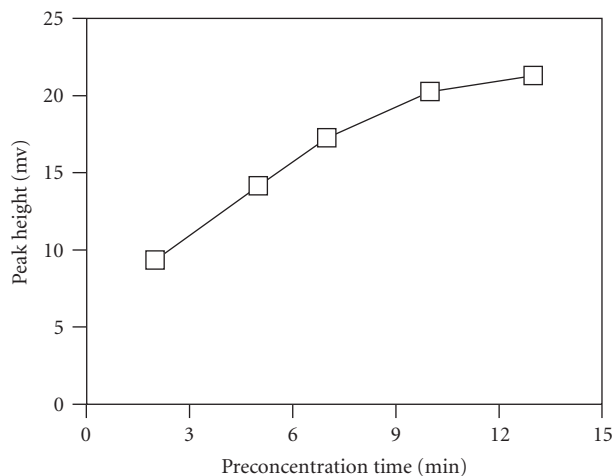


FIGURE 5: Effect of preconcentration time on the peak height.

column which would cause leakage or pump pipes rupture. Too low-preconcentration rate would reduce analysis sensitivity and sampling frequency but augment the preconcentration time. Taken a comprehensive consideration of analysis sensitivity and sampling frequency, preconcentration rate of  $1.5 \text{ min L}^{-1}$  was chosen for further work.

### 3.2.4. Effect of eluent concentration

If eluent concentration was too low, Zn (II) in preconcentration column would elute incompletely. If eluent concentration was too high, it would waste reagent. In the study, nitric acid and oxalic acid-citric acid-lithium hydroxide were tested as eluents. The experimental results showed the sensitivity of the eluent of oxalic acid-citric acid-lithium hydroxide was higher than that of nitric acid. Thus, oxalic acid-citric acid-lithium hydroxide was selected as eluent solution and its concentrations were  $0.01 \text{ mol L}^{-1}$ ,  $0.0075 \text{ mol L}^{-1}$  and  $0.05 \text{ mol L}^{-1}$ , respectively.

### 3.2.5. Effect of eluent flow rate

The sensitivity was greatly affected by flow rate of eluent. If flow rate was too high, the sensitivity augmented and baseline noises increased. If flow rate was too slow, Zn (II) in concentration column would elute incompletely, which caused sensitivity decline. The result showed that flow rate of  $0.5 \text{ mL min}^{-1}$  of eluent was optimal for further work.

### 3.3. Effects of foreign ions

The interference of some possibly coexisting foreign metallic ions was examined to make sure the proposed method can be applied to determine Zn (II) in water. The tolerance limit was defined as the concentration of added solutions causing less than  $\pm 5\%$  relative error during the determination of  $10 \mu\text{g L}^{-1}$  of Zn (II). No interference was observed from a great deal of  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Cr}^{6+}$ ,  $\text{Al}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{As}^{3+}$ , and so forth. However, the metallic ions of  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{2+}$  interfered.

TABLE 1: Determination of zinc in water samples by the proposed method.

Sample	Measured ( $\mu\text{g L}^{-1}$ )	Spiked ( $\mu\text{g L}^{-1}$ )	Found ( $\mu\text{g L}^{-1}$ )	Recovery (%)
River water 1#	38.50	30.00	67.63	97.1
River water 2#	59.26	50.00	108.56	98.6
Lake water	4.48	5.00	9.72	104.8
Spring water	7.26	10.00	17.12	98.6

The interference was eliminated ( $100 \mu\text{g L}^{-1}$  of each ion of  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Fe}^{2+}$ ) by adding 1.5 mL of 10% sodium hexametaphosphate, 1 mL of 0.1% DDTc, and 2 mL of o-phenanthroline as appropriate masking reagents into mixed chromogenic reagent solution. Thus, the results showed that the proposed method had good selectivity.

### 3.4. Linearity, precision, and detection limit of the proposed method

To assess the reproducibility and accuracy of the proposed method, under the selected conditions above, tests of linearity, precision, and detection limit were conducted. The linearity was tested by a series of working standard solutions of Zn (II) ranging from  $0.5 \mu\text{g L}^{-1}$  to  $400 \mu\text{g L}^{-1}$ . Test showed that the peak height versus Zn (II) concentration was linear within the range of  $2.0 \text{ g L}^{-1}$  to  $360 \mu\text{g L}^{-1}$ . The curve was  $H = 0.427C + 3.638$  (H: peak height; C: concentration of Zn (II) ( $\mu\text{g L}^{-1}$ )) and the correlation coefficient obtained was 0.9995 and the detection limit (3 multiples of baseline noises) was  $0.42 \mu\text{g L}^{-1}$ . The test of precision was conducted by eight injections of  $5.0 \mu\text{g L}^{-1}$  and  $50 \mu\text{g L}^{-1}$  of Zn (II) standard solution, respectively. The results showed that the relative standard deviation (RSD) was calculated as 3.55% and 2.14%, respectively.

### 3.5. Application

The proposed method was applied to determine Zn (II) in water samples using the ZJ-la automatic metallic element analyzer. The analysis results of samples were shown in Table 1.

To prove the accuracy of the method, a test of recovery would be conducted by accurately adding known concentration of Zn (II) into sample whose original Zn (II) had been determined. The test results in Table 1 showed that the recovery was between 97.1% and 104.8% and analytical results of the proposed method were satisfactory. Therefore, the proposed method was suitable for determination of trace amounts of Zn (II) in water.

## 4. CONCLUSION

The proposed method was significant with regard to the development of a simple, reliable, and sensitive flow injection method for online preconcentration and determination of trace amounts of zinc (II). High sensitivity, selectivity, broad determination range ( $2.0 \mu\text{g L}^{-1}$  to  $360 \mu\text{g L}^{-1}$ ) of Zn (II), low-detection limit ( $0.42 \mu\text{g L}^{-1}$ ), and fully automated

analysis were just some of the advantages of the proposed method. Especially, compared with other existing methods of zinc preconcentration, eluent concentration is even low to  $\text{mmol L}^{-1}$ . The detection limit of the proposed method can be further improved by increasing preconcentration time. The model ZJ-la automatic metallic elements analyzer employed in this study was cheap, small, and easy to move. The proposed method has been successfully applied to determine zinc (II) in water. The method is suitable for determination of Zn (II) in both water samples and other samples for its good selectivity and the above mentioned advantages.

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