Determination of Trace zinc by Fluorescence Spectrophotometry with Bis-sulfosalophen

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Abstract: A new schiff's base bis-sulfosalophen has been synthesized by Sodium salicylaldimine-5-sulphonate with 3,3',4,4'-Biphenyltetramine. Zonic ion can coordinate with the compound and enhance its fluorescence intensity. Thereby, a new spectrofluorimetric method for the determination of trace zonic has been developed. When the concentration of zonic is in the range of 1~7μg/mL, it has a good linear relationship with *F*, where the regression equation and the correlation coefficient are F=205.7+282.6c_{Zn}(μg/mL) and r=0.9935 respectively. The detection limit for zonic has been found to be 1.72ng/mL. The method has been used to determine trace zonic in river, city and mineral water samples with the relative standard deviation of 0.23~3.84%(n=5), the recovery of 101.7~105.0%.

1.Introduction

Salophen is a condensation polyer by salicylaldehyde and o-phenylenediamine. It is a kind of schiff base with C=N groups, planar, rigid, large p conjugated and fluorescence characteristic, which can be used to coordinate with metal ions as a chelating agent. The color reaction and fluorescence characteristics of the complexes can be used to determine the content of metal ions [1-4], but their selectivity and sensitivity are not satisfactory. Bis-salophen condensated by salicylic aldehyde with 3,3',4,4'-Biphenyltetramine shows stronger recognition and affinity to metal ions. It's functions are superior to the former. At present, the studies on bis-salophen and metal ion complexes are mainly reflected on the application of asymmetric catalysis[5-6], the cleavage and antibacterial activity of DNA[7-8], and the self-assembly properties [9-10], etc. However, it has not been reported on the detection of metal ions. The affinity of bis-sulfosalophen to metal ions is equivalent to that of bis-Salophen. It is easy to be prepared and detected in the aqueous solution. At present, the study of bis-sulfosalophen is mainly on uranyl coordination and fluorescence characteristics [11-13]. But the detection of zonic ions in water has not been reported. In this paper, Bis-sulfosalophen is condensated by Sodium salicylaldimine-5-sulphonate and 3,3',4,4'-Biphenyltetramine, then coordinated with Zn^{2+}. Based on the characteristics of fluorescence intensity enhancing, an accurate method for the determination of trace zonic is established. The method is simple, rapid and sensitive. It is suitable for the determination of zonic in river water, tap water and mineral water.

2.Emperment

2.1 Some importent instruments

Fluorescence spectrophotometer: HitachiF-4500, Hitachi Company of Japan, excitation light source is xenon solitary lamp, phototube voltage of 700V, response speed of 2.0S, slit width of 5.0 nm, wavelength scanning in the range of 200~900nm.

Fourier transform infrared spectrometer: IR-Prestige-21 type, Japan Shimadzu company, scanning wavelength in the range of 4000~400cm^{-1}, mirror surface is experimental background, resolution of 8cm^{-1}, scanning 20 times.

Element analyzer: Flash EA112, American Thermal Power Company, the range of determination is 100ppm, accuracy ≤ 0.3, balance range of 0.1~2.1g, sample quantity of 10mg, analysis time of 8 minutes.

2.2 Some important reagents

Bis-sulfosalophen solution: 0.1034gBSS solids were weighed accurately, dissolved and diluted with secondary distilled water, transferred to 100mL capacity bottle, then fixed volume to the scale of capacity bottle, shaked well. 500μL of the solutions taked accurately were transferred to the 100 mL volumetric bottle, and then the second distilled water was used to fix the volume to the scale of the capacity bottle, and then the 5nmol/mL BSS solution of was obtained by rocking.

Zonic standard solution: 0.2468g standard zonic sulfate ($ZnSO_4$) were dissolved in water, acidified with a few drops of sulfuric acid, diluted to 1000ml with water, the concentration of the solution is 1 mmol/L, then diluted.

Buffer solution was mixed by 0.1mol/L$NH_3.H_2O$ with 0.18mol/LNH_4Cl, its pH is 9.0.

The water of the experiment is secondary distilled water.

2.3 Synthesis of reagents

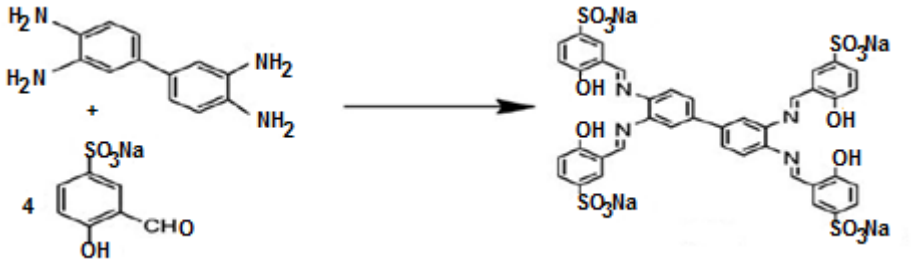

Fig. 1 Synthesising of bis-sulfosalophen (BSS)

Bis-sulfosalophen (BSS), a bipolar quadrudentate ligand, was designed and synthesized by schiff base's condensation reaction. 0.22g(1mmol) 3,3',4,4'-Biphenyltetramine were dissolved in 50mL anhydrous methanol, then 50mL 0.90g(4mmol) Sodium salicylaldimine-5-sulphonate solution with methanol as solvent were added. The mixture was refluxed and stirred for 5 hours at 70℃. After rotary evaporation, the solid product was obtained after cooling to room temperature. The solid product was then filtered, then recrystallized with anhydrous ethanol and dried in vacuum.

2.4 Experimental procedure

During the experiment, a certain amount of zonic standard solution were divided into 10ml capacity bottle, 1ml pH 9.0 buffer solution were added, 1.0 ml BSS solution were added while stirring, and diluted with water to scale and shake well. The fluorescence intensity of the solution was measured at λex = 355 nm.

3.results and discussions

3.1 Elemental analysis

The obtained BSS was analyzed elementarily, and the results are shown in Table 1. It can be seen from the table that the experimental value of the mass fraction of C、H、N is basically consistent with the theoretical value, and it can be preliminarily proved that the obtained product is the target product.

Table 1 Elemental analysis of $C_{40}H_{26}N_4Na_4O_{16}S_4$

$C_{40}H_{26}N_4Na_4O_{16}S_4$	C	H	N
Theoretical	46.24	2.52	5.39
Experimental	46.36	2.63	5.24

3.2 Infrared spectrum analysis

Fig.2 shows the infrared spectra of bis-sulfosalophen. The absorption band of ligand appears at 1034 cm^{-1}, which can be classified as σ (- SO_3). At 1618 cm^{-1}, it is assigned to C=N stretching vibration, and the ligand phenolic hydroxyl stretching band ν_{OH} (phenol) is located at 3454 cm^{-1}.

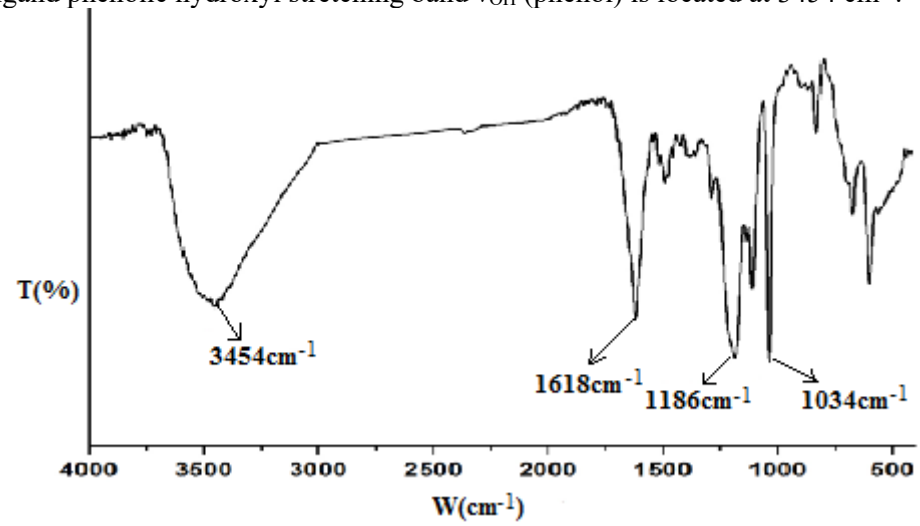

Fig. 2 IR spectrum of bis-sulfosalophen (BSS).

The vibrational types of the absorption peaks are classified in Table 2. It shows that the main functional groups in the molecular structure of bis-sulfosalophen are C=N、-OH、C-O、-SO_3.

Table 2 Absorption peak data in IR spectrum of bis-sulfosalophen(BSS)

Compound	$\nu_{C=N}$	ν_{OH}	ν_{C-O}	σ(-SO_3)
Bis-sulfosalophen	1618	3454	1186	1034

3.3 Fluorescence spectra of bis-sulfosalophen reagent and complex

Fig.3 shows the excitation and emission spectra of bis-sulfosalophen. The maximum wavelengths of excitation and emission are 255.0nm and 355.2nm respectively. Fig.4 shows the emission spectra of bis-sulfosalophen and zonic complexes at the maximum excitation wavelength. The range of c_{Zn} is from 1 to 7μg/mL. It can be seen from the diagram that the fluorescence intensity F is enhancing with the increasing of c_{Zn}, So the linear relationship between c_{Zn} and F can be established.

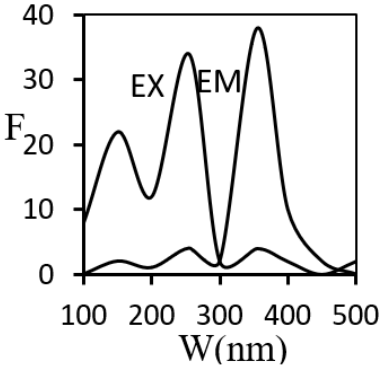

Fig.3 Excitation and Emission spectra of bis-sulfosalophen
EX of excitation spectrum and EM of emission spectrum.

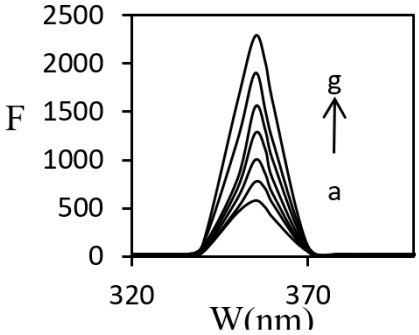

Fig. 4 Emission spectra of bis(sulfo)Zn-salophen complexes
c_{BSS}: 5 nmol / mL, c_{Zn}: a→g 1,2,3,4,5,6,7(μg/mL)

3.4 Effect of pH value on the reaction

The reaction of Zn^{2+} with the reagent is related to the pH value. When pH < 7.8, the reagent is easy to be protonated, which affects the coordination effect. When pH > 9.6, Zn^{2+} is easy to be hydrolyzed. So the optimum pH value range is 7.8-9.6, In addition, the selection of buffer system was investigated. The phosphate buffer system is the most commonly used, but the phosphate buffer system can not be used in this study because of the strong coordination ability between phosphate and zonic. The results show that NH_3-NH_4Cl buffer has no effect on the coordination reaction between zonic and BSS. Therefore, the NH_3-NH_4Cl buffer of pH 9.0 was selected.

3.5 Selection of experimental conditions

The adding order of Zn^{2+} and BSS was tested. The results show compared with zonic ions added to the BSS solution, BSS added to the zonic ion solution has the stronger fluorescence emission signal.

The influence of reaction time on the fluorescence intensity of the system was investigated. Table 3 shows that when the reaction time is 15 minutes, the fluorescence intensity can reach the maximum and remain basically unchanged. Therefore, BSS was selected to react with zonic for 15 minutes, and then the fluorescence changes were detected.

Table 3 The influence of time on fluorescence intensity

Time（min）	5	10	15	20	25	30
F	524	765	825	825	824	824

3.6 Working curve

According to the experimental steps, the standard working curve is drawn with c_{Zn} as the transverse coordinate and the fluorescence intensity *F* as the vertical coordinate. When c_{Zn} was in the range of 1~7μg/mL, there was a good linear relationship with *F*, and the regression equation and correlation coefficient are F=205.7+282.6c_{Zn}(μg/mL) and r = 0.9935 respectively, The detection limit of the method is 1.72 ng/mL.

3.7 Effect of some coexistent ions

The interferences of some coexistent common anions and cations to the reaction system was investigated. When the relative error was less than ±5%, and 6.4μg/mL zonic was added to the system. The results show that the maximum allowable multiple of some coexistent ions are K^+(600), Pb^{2+}(2), Zn^{2+}(14), Cr^{2+}(1.8), Ba^{2+},Cd^{2+}(13), Mg^{2+}(16), Ca^{2+}(11), Sr^{2+}(1), Mn^{2+}(3), NO_2^-(35), CO_3^{2-}(30), $C_2O_4^{2-}$(1.7), F^-(72), Al^{3+}(0.3), Fe^{3+}(0.4). Therefore, except Fe^{3+} and Al^{3+}, the other ions have higher allowable amount. When

0.5mL 0.1% (mass fraction) NaF is added, this can be determined directly.

3.8 Precision test

The river water, tap water and mineral water were determined according to the experimental method. The measured data are listed in Table 4. The results show that the precision is good, the relative standard deviation is 0.23~3.84%.

Table 4 Results of precision test (n=5)

Sample(5ml)	Measurement (μg)	Average (μg)	RSD%
River water	22.28,22.31,22.35,22.38,22.41	22.35	0.23
Tap water	4.98,5.05,5.08,5.16,5.22	5.10	1.84
Mineral water	0.21,0.20,0.22,0.23,0.22	0.22	3.84

3.9 Recovery test

20g and 0.2g zonic ions were added to 5ml river water, tap water and mineral water samples respectively. The determination results are shown in Table 4. The recovery rate of zonic is 101.7%~ 105.0%.

Table 5 Results of standard addition recovery test

Sample（5ml）	Initial(μg)	Addition(μg)	Measurement(μg)	Recovery(%)
River water	22.35	20	42.69	101.7
Tap water	5.10	5.0	10.22	102.4
Mineral water	0.22	0.20	0.43	105.0

4.Conclusion

In this paper, a new method for the determination of trace zonic was established based on the characteristics of bis(sulfo)Zn-Salophen complex's fluorescence enchancing. The detection limit, precision and accuracy of the method were analyzed. The experiment shows that the method is simple, accurate and easy to be popularized.

Acknowledgement

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