

# Determination of Dissolved Oxygen in Water Based on Its Quenching Effect on the Fluorescent Intensity of Bis(2,2'-bipyridine)-5-amino-1,10-phenanthroline Ruthenium Complex

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A water-soluble fluorescence dye, bis(2,2'-bipyridine)-5-amino-1,10-phenanthroline ruthenium complex (Ru(bpy)<sub>2</sub>-(5-NH<sub>2</sub>-1,10-phen)), was synthesized and used as a fluorescence probe for detecting dissolved oxygen in water. The fluorescence intensity of the probe in different dissolved-oxygen concentrations was investigated. The sensitivity of the probe was evaluated in terms of the ratio  $I_N/I_{O_2}$ , where  $I_N$  and  $I_{O_2}$  correspond to the detected fluorescence intensity of nitrogen and oxygen-saturated solutions, respectively. The experimental results showed that the probe yielded a linear Stern-Volmer plot, and had a  $I_N/I_{O_2}$  ratio of about 5.2. The detection limit, defined as three-times the standard deviation, was  $8.6 \times 10^{-7}$  mol L<sup>-1</sup> after eleven determinations of nitrogen-saturated blank solutions. Additionally, the probe was pH-insensitive and ionic strength-independent with good characteristics of practicality and selectivity.

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## Introduction

Oxygen, a reactive molecule in nature, is one of the most important chemical agents in our life. The determination of the dissolved oxygen level has been of great interest, and has been studied over the past few decades in biotechnology, environmental monitoring, medicine and the chemical industry.<sup>1-5</sup> Various methods and techniques have been proposed for the determination of dissolved oxygen. The main approaches of dissolved-oxygen concentration measurements are the Winkler iodometric titration method,<sup>6</sup> the electrochemical method,<sup>7</sup> and the optical method (based on luminescence quenching).<sup>8</sup>

Due to high accuracy and simple operation, the Winkler iodometric titration method has been the standard iodometric method for the determination of dissolved oxygen. It has been modified and improved regarding the disadvantages of time-consuming for operation and skillful technique requiring by Sakai *et al.*,<sup>9</sup> who described an off-line Winkler's method coupled with flow-injection analysis and an automatic flow system with in-line Winkler's procedure for the determination of dissolved oxygen in environmental water. However it also has disadvantages of a narrow linear range of measurements and interference from other common coexisting species. At the present time, the most common method for dissolved-oxygen detection is based on electrochemical techniques. Though the electrochemical method has the characteristics of high sensitivity and operational simplicity, the electrode is easily poisoned, which limits the service time and the accuracy, especially in

corrosive environments.

Among these various determination methods, an optical method based on the quenching of the fluorescence of dyes by oxygen has attracted intense attention. It provides an alternative to conventional methods for having the advantages of versatility, high sensitivity as well as low toxicity.<sup>10</sup> The fluorescence quenching of oxygen-sensitive dyes is closely correlated with the oxygen concentration using Stern-Volmer kinetic analysis.<sup>11</sup> The luminescence decay time and luminescence intensity both vary as a function of the oxygen concentration; both parameters provide a feasible measurement index. Considerable approaches based on the luminescence intensity and decay time have been presented.<sup>12-17</sup>

The property of fluorophore used for oxygen sensing is a primary factor. Luminescent transition-metal complexes, especially ruthenium diimine complexes, reveal considerably high photostability, large Stokes shifts and high quenching efficiencies. As a result, the ruthenium diimine complexes have become a kind of the most suitable fluorophores for an oxygen indicator. Dissolved ruthenium complexes, Ru(bpy)<sub>3</sub> (bpy = 2,2'-bipyridine) and Ru(phen)<sub>3</sub> (phen = 1,10-phenanthroline) were used as luminescent probes for measuring oxygen in individual intact cells.<sup>18</sup> Ru(bpy)<sub>3</sub> fragments were also covalently grafted to a sol-gel derived thin film and used for monitoring the dissolved oxygen in the liquid phase, and the ratio  $I_N/I_{O_2}$  is 4.3.<sup>19</sup> Rosenzweig *et al.*<sup>20</sup> reported a submicrometer optical fiber sensor based on Ru(phen)<sub>3</sub> for dissolved oxygen measurements. However, the leaching of dye from the sensor limits the use of time, which affects the accuracy. There are also some other ruthenium complexes used as probes, or for preparing sensors to detect dissolved oxygen.<sup>21</sup> Though those complexes have been successfully used for oxygen sensing,

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it is of interest to find a high-sensitivity, wide detection range method.

In this paper, a ruthenium complex,  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$ , which was also used for fabricating electrochemiluminescence sensors by Chen *et al.*,<sup>22,23</sup> was synthesized and used as an oxygen probe for dissolved-oxygen concentration determination. The authors also investigated the oxygen response of two other typical ruthenium complexes,  $\text{Ru}(\text{phen})_3$  and  $\text{Ru}(5\text{-NH}_2\text{-1,10-phen})_3$ . By comparing and analyzing the luminescence spectra of the three complexes, the authors found that  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$  had stronger luminescence, better oxygen quenching efficiencies and high sensitivity. Those it applicable to quantify dissolved oxygen in water. The Stern-Volmer quenching constant ( $K_{\text{sv}}$ ) is greater than that which has been presented,<sup>2,13,19</sup> and found to be  $0.166 \text{ L mg}^{-1}$  with a correlation coefficient of 0.9988 in the linear range from 0.1 to  $14.5 \text{ mg L}^{-1}$  dissolved oxygen. This approach has the characteristics of simplicity, wide range of linearity, high sensitivity and selectivity.

## Experimental

### Materials and reagents

Ruthenium chloride, 2,2'-bipyridyl and *N,N*-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). Tri(1,10-phenanthroline) ruthenium chloride hydrate was purchased from Aldrich (USA). Sodium perchlorate ( $\text{NaClO}_4$ ) was purchased from Kernel Chemical Reagent Co. (China, Tianjin). 5-NH<sub>2</sub>-1,10-phenanthroline was synthesized according to the literature.<sup>24</sup> Britton-Robinson (B-R) buffer solutions in the pH range of 1.81 – 11.98 were prepared by mixing appropriate amounts of acetic, boric acid and phosphoric of the same concentration ( $0.04 \text{ mol L}^{-1}$ ), and adjusting to the desired pH with  $0.2 \text{ mol L}^{-1}$  sodium hydroxide. Outside this range, the pH was adjusted by adding a HCl ( $1 \text{ mol L}^{-1}$ ) or NaOH ( $1 \text{ mol L}^{-1}$ ) solution. Unless otherwise stated, all other reagents were of analytical reagent grade and were used as received without further purification. Double distilled water was used in the preparation of all aqueous solutions.

### The synthesis of $\text{Ru}(5\text{-NH}_2\text{-1,10-phen})_3$ and $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$

$\text{Ru}(5\text{-NH}_2\text{-1,10-phen})_3$  was prepared as described in the literature.<sup>25</sup>  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$  was synthesized as previously described with modification. Commercial  $\text{RuCl}_3$  (130.8 mg, 0.63 mmol), bipyridine (197.0 mg, 1.26 mmol), and LiCl (2 mg) were dissolved in 10 mL DMF; the mixture was deaerated with nitrogen for 30 min and then heated at reflux for 8 h under nitrogen. The reaction mixture was stirred magnetically throughout this period. After the reaction mixture was cooled to room temperature, 100 mL of acetone was added, and the resultant solution cooled at  $0^\circ\text{C}$  overnight. Then, the violet-black precipitate was filtered and washed with distilled water three times to remove impurities, and dried overnight under a vacuum. The product,  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ , was obtained in 55% yield.

The complexation reaction of  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and 5-NH<sub>2</sub>-phen as the second ligand was as follows. A 10% molar excess of 5-amino-1,10-phenanthroline (85.9 mg, 0.44 mmol) dissolved in 10 mL ethanol was added to 5 mL of H<sub>2</sub>O contained  $\text{Ru}(\text{bpy})_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  (208.2 mg, 0.4 mmol). The mixture was heated at reflux for 3 h under nitrogen. Upon completion of the reaction, most of the ethanol was evaporated under reduced pressure, and a 10-fold molar excess of  $\text{NaClO}_4$  was added to

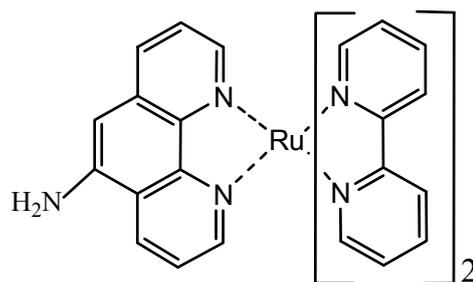


Fig. 1 Formula of complex  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$ .

produce an orangish precipitate. The precipitate was filtered and purified by elution chromatography on an alumina column with a 2:1 toluene-acetonitrile solution. After elution and evaporation, the product was washed with diethyl ether three times, and dried overnight under a vacuum. The complex  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$  was obtained in about 67% yield. It was water soluble; 1 mg of it can be completely dissolved in 1 ml of water. The formula of the complex was in Fig. 1. <sup>1</sup>H NMR (400 MHz,  $\delta$  ppm, DMSO):  $\delta$  8.82 – 8.74 (m, 4H),  $\delta$  8.33 – 8.31 (d, 2H,  $J = 8.8 \text{ Hz}$ ),  $\delta$  8.22 – 8.17 (m, 2H),  $\delta$  8.11 – 8.09 (t, 4H,  $J = 7.6 \text{ Hz}$ ),  $\delta$  7.85 – 7.80 (m, 4H),  $\delta$  7.61 – 7.56 (m, 4H),  $\delta$  7.40 – 7.37 (m, 2H),  $\delta$  6.95 (s, 1H),  $\delta$  2.51 (s, 2H). The ternary complex was further characterized through IR and elemental analysis. The  $\nu_{(\text{C}=\text{N})}$  stretching vibrations in the infrared spectrum at 1595, 1429  $\text{cm}^{-1}$  of 5-NH<sub>2</sub>-1,10-phen and 1579, 1456  $\text{cm}^{-1}$  of 2,2'-bipyridine were changed to 1582, 1433  $\text{cm}^{-1}$  in the spectrum of the complex. Elemental analysis (calculated/found) for the dye  $[\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  ( $\text{C}_{32}\text{H}_{27}\text{N}_7\text{O}_9\text{Cl}_2\text{Ru}$ ): C, 46.84/46.56; H, 3.45/3.30; N, 11.76/11.88.

### Instrumentation

A Perkin-Elmer LS-55 spectrofluorometer equipped with a pulsed Xe lamp was used to conduct all fluorescence measurements. The measurements were controlled by a personal computer data-processing unit with both excitation and emission slits set at 10 nm. All aqueous solution pH values were measured by using a PHS-3B pH meter (Shanghai Analytical Instruments, China), which was adjusted with standard buffers before use. A JPB-607 dissolved-oxygen meter (Shanghai Analytical Instruments, China) was used for dissolved-oxygen concentration measurements. Unless otherwise specified, all measurements in the experiment were carried out at room temperature ( $20^\circ\text{C}$ ) and atmospheric pressure.

## Results and Discussion

### Fluorescence spectral properties and oxygen response of ruthenium complexes

$\text{Ru}(5\text{-NH}_2\text{-1,10-phen})_3$ ,  $\text{Ru}(\text{phen})_3$  and  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$  have a similar molar absorptivity and different fluorescence quantum yields at 610 nm. The excitation wavelengths of  $\text{Ru}(5\text{-NH}_2\text{-1,10-phen})_3$ ,  $\text{Ru}(\text{phen})_3$  and  $\text{Ru}(\text{bpy})_2(5\text{-NH}_2\text{-1,10-phen})$  was 460, 450 and 460 nm, respectively. A comparison between the responses of these three complexes to dissolved molecular oxygen is shown in Fig. 2. The luminescence intensity of these three complexes at  $5 \times 10^{-5} \text{ mol L}^{-1}$  was determined in oxygen, air and nitrogen-saturated solutions, respectively. It can be seen

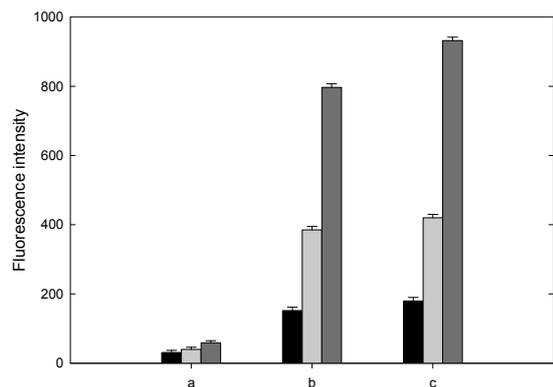


Fig. 2 Fluorescence intensity of: (a) Ru(5-NH<sub>2</sub>-1,10-Phen)<sub>3</sub>, (b) Ru(phen)<sub>3</sub>, and (c) Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen), measured in nitrogen (■), air (▒) and oxygen-saturated (□) solutions. The concentration of the three complexes is  $5 \times 10^{-5}$  mol L<sup>-1</sup>, and the excitation wavelength is 460, 450 and 460 nm, respectively.

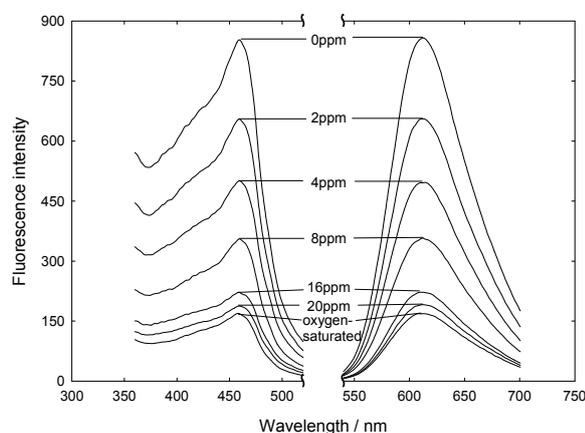


Fig. 3 Fluorescence spectra of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) measured in 0, 2, 4, 8, 16, 20 mg L<sup>-1</sup> dissolved oxygen and oxygen-saturated solutions; 1 ppm equivalent of 1 mg L<sup>-1</sup> or  $3.125 \times 10^{-5}$  mol L<sup>-1</sup>; the concentration of the probe is  $2 \times 10^{-5}$  mol L<sup>-1</sup>.

that the sensitivity of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) in terms of the ratio  $I_{N_2}/I_{O_2}$  ( $I_{N_2}/I_{O_2}$  about 5.2) is equivalent to that of Ru(phen)<sub>3</sub>, and more than twice than that of Ru(5-NH<sub>2</sub>-1,10-phen)<sub>3</sub>. Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) has the strongest luminescence intensity at a low complex concentration under the same conditions.

#### Spectral changes with different oxygen concentrations

The fluorescence spectra of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) in a neutral aqueous solution with different oxygen concentrations is shown in Fig. 3. The concentration of the probe is  $2 \times 10^{-5}$  mol L<sup>-1</sup>. It is clear that the fluorescence intensity decreases with the increase of the oxygen concentration. The relative change in the fluorescence intensity from 2 to 4 mg L<sup>-1</sup>, 4 to 8 mg L<sup>-1</sup> is comparable with the change in the fluorescence intensity from 8 to 16 mg L<sup>-1</sup> dissolved oxygen. When the dissolved-oxygen concentration is more than 16 mg L<sup>-1</sup>, the relative change in the fluorescence intensity per oxygen concentration interval is inconspicuous.

Table 1 Interference of different substances in the fluorescence intensity of the oxygen probe

Interferent	Concentration/ mol L <sup>-1</sup>	Relative fluorescence intensity change (%)/ $\Delta F/F_0 \times 100$
NaCl	$1 \times 10^{-2}$	1.16
NaAc	$1 \times 10^{-2}$	0.05
NaBr	$1 \times 10^{-2}$	-0.08
BaCl <sub>2</sub>	$1 \times 10^{-3}$	2.37
CoCl <sub>2</sub>	$1 \times 10^{-3}$	-1.33
Zn(Ac) <sub>2</sub>	$1 \times 10^{-3}$	-0.41
Pb(Ac) <sub>2</sub>	$1 \times 10^{-3}$	1.12
Na <sub>2</sub> SO <sub>3</sub>	$1 \times 10^{-2}$	-1.25
Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	$1 \times 10^{-3}$	-0.04
CuSO <sub>4</sub>	$1 \times 10^{-2}$	-3.94
Ni(NO <sub>3</sub> ) <sub>2</sub>	$1 \times 10^{-3}$	2.10
Cr(NO <sub>3</sub> ) <sub>3</sub>	$1 \times 10^{-3}$	0.56
NaClO <sub>4</sub>	$1 \times 10^{-2}$	3.49
NaSCN	$1 \times 10^{-2}$	-0.27
Urea	$1 \times 10^{-3}$	-0.68
Phenol	$1 \times 10^{-3}$	-0.04
Benzoic acid	$1 \times 10^{-3}$	0.05
Trisodium citrate	$1 \times 10^{-3}$	-1.1
SDS	$1 \times 10^{-2}$	2.64
Tetramethylammonium bromide	$1 \times 10^{-2}$	0.16
Hydroxylamine hydrochloride	$1 \times 10^{-2}$	1.15

$\Delta F = F - F_0$ ,  $F_0$  and  $F$  are the fluorescence intensity of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) ( $2 \times 10^{-5}$  mol L<sup>-1</sup>) in aqueous solution without and with interferents, respectively. The excitation and emission wavelength is 460 and 610 nm, respectively.

#### Selectivity

The interference of common species present in the environment in fluorescence measurements of dissolved oxygen was investigated. The experiment was performed by using a neutral aqueous solution with a probe concentration of  $2 \times 10^{-5}$  mol L<sup>-1</sup>, and then recording the changes of the fluorescence intensity in both the absence and presence of interferents. The results are given in Table 1. For common inorganic ions and some possible coexisting organics, the relative errors were less than 3.94%, which was considered to be tolerable. Therefore, the probe would not be affected by common species, which made it feasible for practical applications.

#### The effect of pH on fluorescence intensity

The pH is an important factor correlating the performance of fluorescence dyes in aqueous media. The effect of the pH was investigated by examining the fluorescence intensity at different pH values with a probe concentration of  $2 \times 10^{-5}$  mol L<sup>-1</sup>. The acidity of solutions was maintained by using B-R buffer solutions in the range of 1.81 to 11.98; outside this range the pH was adjusted by adding HCl or NaOH. Figure 4 shows the effect of the pH on fluorescence intensity. It was clearly that the luminescence of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) was pH-independent of between pH 1.8 and 13. When outside this range the fluorescence intensity decreased rapidly; the complex may have been destroyed under highly acid or alkaline conditions. Consequently, we could carry out measurements of most water samples without any pH adjustment, except under highly acid or alkaline conditions.

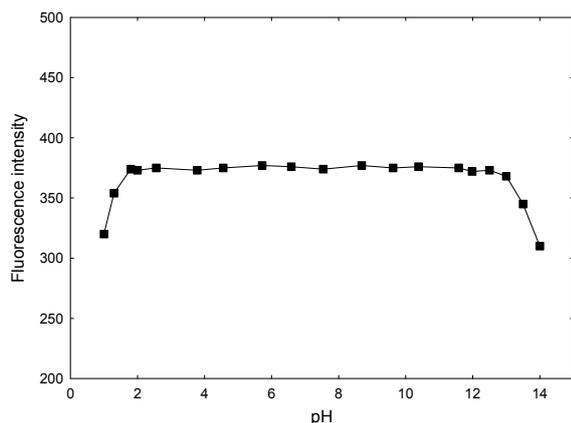


Fig. 4 pH effect on the fluorescence intensity:  $2 \times 10^{-5}$  mol L<sup>-1</sup> Ru(5-NH<sub>2</sub>-1,10-Phen)<sub>3</sub> in B-R buffer solutions in the range of pH 1.81 to 11.98; outside this range the pH was adjusted by the addition of HCl or NaOH.

#### Effect of ionic strength

The ionic strength is considered to be a critical influence factor of a fluorescence intensity measurement in an aqueous solution. Solutions were adjusted to contain different concentrations of NaCl, from 0.01 to 2 mol L<sup>-1</sup>. It was found that there was no significant change in the fluorescence intensity with increasing ionic strength. The relative error of the fluorescence intensity was less than 0.68% in the range of NaCl from 0.01 to 2 mol L<sup>-1</sup>. Therefore, the fluorescence intensity was considered to be constant, and the effect of the ionic strength on an oxygen measurement could be neglected.

#### Quantification and detection limit

An optical measurement based on fluorescence quenching was examined by the Stern-Volmer equation.<sup>11</sup> Equation (1) gives the relationship between the fluorescence intensity ( $I_C$ ) and the dissolved oxygen concentration [ $O_2$ ],

$$I_0/I_C = 1 + K_{SV}[O_2], \quad (1)$$

where  $I_0$  is the fluorescence intensity in a nitrogen-saturated solution,  $I_C$  the fluorescence intensity in a given dissolved oxygen concentration solution, and  $K_{SV}$  the Stern-Volmer quenching constant. The analytical range of different oxygen probes is decided by the respective Stern-Volmer constant and the quenching curve. In principle, a higher quenching constant better accuracy at low levels of dissolved oxygen as a result of the larger relative signal change per oxygen concentration interval. However, high quenching constants limit the linear dynamic range. The authors found that the linear range of Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) is between 0.1 to 14.5 mg L<sup>-1</sup> dissolved oxygen. Outside this range, a big deviation from linearity was observed. The results are shown in Fig. 5. In the linear range, the experimental data fitted a calibration equation of the form,

$$I_0/I_C = 1.015 + 0.166[O_2] \quad (r = 0.9988), \quad (2)$$

The standard error of the intercept and the slope of the regression are 0.03 and 0.0031, respectively. The equation provides a quantitative basis for the determination of dissolved oxygen in water. Here, the concentration of  $O_2$  was measured by JPB-607, which can include standard errors of  $\pm 0.1$  mg L<sup>-1</sup>, which was

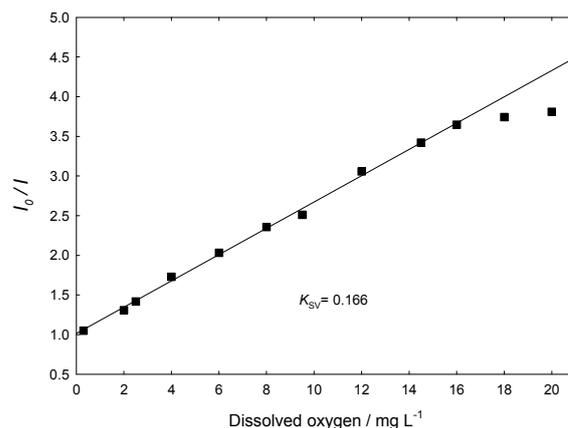


Fig. 5 Stern-Volmer plot of Ru(5-NH<sub>2</sub>-1,10-Phen)<sub>3</sub> dissolved in an aqueous solution,  $K_{SV} = 0.166$  L mg<sup>-1</sup>, with a correlation coefficient of 0.9988 between 0.1 and 14.5 mg L<sup>-1</sup>.

Table 2 Concentrations of dissolved oxygen in three sample solutions determined by the newly proposed fluorescent method and the dissolved oxygen meter

Sample <sup>a</sup>	Do <sup>b</sup> /mg L <sup>-1</sup>	Do <sup>c</sup> /mg L <sup>-1</sup>	Difference
Waste water	$3.33 \pm 0.12$	$3.2 \pm 0.3$	0.13
Tap water	$9.26 \pm 0.17$	$9.1 \pm 0.3$	0.16
River water	$6.65 \pm 0.14$	$6.8 \pm 0.3$	-0.15

a. The measurements were carried out at room temperature (20°C) and atmospheric pressure.

b. Measured by the present method (means of three determinations), the concentration of the probe is  $2 \times 10^{-5}$  mol L<sup>-1</sup>.

c. Measured by the JPB-607 dissolved oxygen meter.

realized in the present study after triplicate measurements. However, in the statistical derivation of Eq. (2), the error in the independent parameter,  $O_2$  concentration, was neglected for simplicity in the data treatment. According to the calibration equation, the detection limit, defined as three-times the standard deviation, was  $8.6 \times 10^{-7}$  mol L<sup>-1</sup> after eleven determinations of the nitrogen-saturated blank solutions.

#### Practical application

In order to evaluate the accuracy of this method, three types of samples including waste water, tap water and river water were determined by using the present new method and the JPB-607 dissolved oxygen meter. No pretreatment was performed prior to analysis sample. Before dissolved-oxygen measurements, the waste-water and river-water samples were allowed to stand for a few hours. The results are compared in Table 2. As can be seen from Table 2, the results obtained by using the new method are in good agreement with that using a dissolved oxygen meter, which indicates that the proposed method is accurate, credible and precise for practical analysis.

## Conclusion

This paper has presented a widely linear, highly sensitive and selective fluorescence probe for dissolved-oxygen concentration measurements. The fluorescence intensity of the probe decreases with the increase of the dissolved-oxygen

concentration. The experimental results have shown that Ru(bpy)<sub>2</sub>(5-NH<sub>2</sub>-1,10-phen) as an oxygen probe has better sensitivity than the other two typical ruthenium complexes. The probe is insensitive to the pH and the ionic strength, and common inorganic ions and some possible coexisting organics affect less the result within a tolerable amount. Therefore, the probe has good characteristics of practicality, sensitivity and selectivity in dissolved-oxygen measurements. The probe can also be used in other fields, such as medicine as well as industrial and environment monitoring domains.

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