Surfactant Enhanced Resonance Rayleigh Scattering Method for the Determination of Dissolved Oxygen in Environmental Water

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A novel method for the determination of trace amounts of dissolved oxygen based on resonance rayleigh scattering (RRS) has been developed. Dissolved oxygen in the water sample was fixed by adding $MnSO_4$ in an alkaline medium to form $Mn(OH)_3$ from which oxygen was liberated upon addition of H_2SO_4 and reacted with the I_3^- liberated by the reaction of KI with H_2SO_4. In the presence of polyvinyl alcohol (PVA), I_3^- reacted with malachite green (MG) to yield I_3^--MG-PVA complex, which results in the enhancement of resonance rayleigh scattering intensity and the appearance of the corresponding resonance rayleigh scattering spectral characteristics. The maximum scatter peak was at 474 nm for the I_3^--MG-PVA system. The enhanced resonance rayleigh scattering intensity was directly proportional to the concentration of I_3^-. On the basis of these reaction, KIO_3, as the standard solution of the dissolved oxygen, reacted with excessive KI and malachite green in the polyvinyl alcohol solution and formed the I_3^--MG-PVA complex. Thus the content of dissolved oxygen could be measured from the standard curve prepared by using KIO_3 standard solution as standard for dissolved oxygen. The optimum conditions of these reactions and the influencing factors have been investigated. In analyzing different water samples, results obtained by the resonance rayleigh scattering method were in consistency with the results obtained by the Winkler method.

Key Words: Resonance rayleigh scattering, Dissolved oxygen, Surfactant.

INTRODUCTION

Dissolved oxygen (DO) is one of the most important substances present in water and it involves in a variety of chemical, biological and biochemical processes in environmental waters. Insufficient concentration of dissolved oxygen in natural waters leads to perishing of higher living organisms. High dissolved oxygen concentration is also very important for the efficiency of wastewater treatment plants. On the other hand oxygen is a strong oxidant and even a low dissolved oxygen concentration in, *e.g.* central heating systems, may lead to premature repairs of the pipelines. It is thus very important to be able to accurately measure dissolved oxygen concentration in water.

Many methods have been proposed for the determination of dissolved oxygen in water since the original work of Winkler[1]. In the late years a lot of researchers put forward other methods for the measurement of dissolved oxygen, such as modified Winkler method[2,3], electrochemical methods[4,5], spectrophotometric method[6-10], the optical sensor method[11,12] and the flow injection method[13,14], *etc*. In these method the Winkler method and electrode method were the mostly used for the dissolved oxygen measurement. The Winkler method (it has been developed as the standard iodometric method[15]

for the determination of dissolved oxygen) has proven precise and robust for determination of dissolved oxygen regardless of the actual matrix components of the sample, *e.g.*, the contents of dissolved salts or organic matter, which in contrast can severely influence the diffusive membrane passage of oxygen when resorting to amperometric detection by the Clark electrode. The electrode further requires a constant approach flow of the sample to the membrane. Due to a considerable delay time and the consumption of dissolved oxygen by the sensor itself, its application to small changes in the concentration or low contents of dissolved oxygen is troublesome.
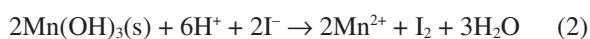
Resonance rayleigh scattering is a special elastic scattering produced when the wavelength of rayleigh scattering (RS) is located at or close to its molecular absorption band. In this case, the frequency of the electromagnetic wave absorbed by the electron is equal to its scattering frequency. It provides new information concerning molecular structure, size, form, charge distribution, state of combination and so on. Therefore, in recent years, this technique has been increasingly applied to the study and determination of biological macromolecules[16,17], trace amounts of inorganic ions[18-21]. Compared with other analytical methods, the resonance rayleigh scattering method possesses the distinct advantages of speed,

convenience, sensitivity and can be accomplished with a common fluorescence spectrometer by using inexpensive and safe reagents. In this paper, we have developed a novel method for the determination of dissolved oxygen based on the formation of I_3^--MG-PVA complex by reaction of I_3^- with malachite green (MG) in presence of polyvinyl alcohol (PVA) and the use of resonance rayleigh scattering technology.

Malachite green, a triphenylmethane dye, is positively charged and has a strong chromophore at 620 nm. It has been widely used around the world as fungicide, ectoparasiticide and antiseptic in the aquaculture. In this paper, we investigated the reaction of I_3^- and malachite green in the presence of some surfactants. The results showed that, in the presence of the polyvinyl alcohol, the associated complex can further react with polyvinyl alcohol to form an I_3^--MG-PVA complex, which can lead to a great enhancement of resonance rayleigh scattering intensity and yield a new complex.

In this paper, a new resonance rayleigh scattering method for determination of dissolved oxygen in water sample based on the I_3^--MG-PVA system was first proposed to determine the content of the dissolved oxygen in environmental water.

The dissolved oxygen in the water could react under alkaline conditions with Mn^{2+} ions forming manganese(III) hydroxide. Then this solution is acidified and Mn^{3+} ions oxidize iodide to iodine, in the presence of excess KI, which eventually forms triiodide. Ralated chemical reactions was as follows:

$$4Mn^{2+} + O_2 + 8OH^- + 2H_2O \rightarrow 4Mn(OH)_3\downarrow \qquad (1)$$

$$2Mn(OH)_3(s) + 6H^+ + 2I^- \rightarrow 2Mn^{2+} + I_2 + 3H_2O \qquad (2)$$

$$I_2 + I^- \rightarrow I_3^- \qquad (3)$$

Then approximate water sample of the formed I_3^- ions which reacted with malachite green in the presence of polyvinyl alcohol to form an ion-associated complex which has a resonance rayleigh scattering intensity at 474 nm. KIO_3 which adopted as the standard solution was used to determine the dissolved oxygen directly and the standardization relied on the preparation of iodate solution. IO_3^- could react with excessive iodide to form I_3^- in the acidic medium. The reaction equation is:

$$IO_3^- + 8I^- + 6H^+ \rightarrow 3I_3^- + 3H_2O \qquad (4)$$
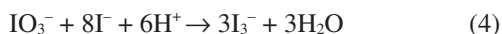
From the reaction (1) to (4) above it could be easily deduced that one mole of iodate equivalent to 3/2 moles of dissolved oxygen in samples(that is to say, IO_3^- of 10 mg/L is equivalent to 2.74 mg/L O_2), so the content of dissolved oxygen could be calculated directly from the work curve prepared by using KIO_3 as standard solution in the I_3^--MG-PVA system, see eqn. (5).

$$\rho_{O_2} = \frac{(I_{RRS} - a)}{b} \times \frac{1.5 \times M_{O_2}}{M_{IO_3^-}} \times \frac{V_1}{V_2} \qquad (5)$$

where ρ = dissolved oxygen concentration(mg/L H_2O); I_{RRS} = resonance rayleigh scattering intensity of I_3^--MG-PVA solution(against the reagent blank); V_1 = the volume of the colour comparison tube; V_2 = sample volume shift from the dissolved oxygen bottle a and b are slope and intercept of the eqn. (6).

$$I_{RRS} = a\rho_{O_2}(mg/L) + b \qquad (6)$$

EXPERIMENTAL

All chemicals were of analytical-reagent grade. All of the reagents were purchased from Shanghai Chemical Reagent Company. All of the solution were prepared by dissolving them in doubly deionized water without further purification. KI: 0.2 mol/L; malachite green: 2.0×10^{-4} mol/L; $MnSO_4$: 0.05 mol/L and 2 mol/L; polyvinyl alcohol (PVA): 10 g/L; acacia gum (AG) : 10 g/L; cetyltrimethylammonium bromide (CTAB): 10 g/L; Tween-60: 10 g/L; sodium dodecyl sulfate (SDS): 10 g/L; The Clark-Lubs buffer solution (C-L) was prepared by adjusting 0.2 mol/L KCl, 0.2 mol/L HCl with 0.2 mol/L potassium acid phthalate. Water used throughout was doubly deionized.

The synchronous fluorescence spectra were performed using a Hitachi F-4500 fluorescence spectrophotometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm).

Collect the water samples with the flask bottle sampler (narrow mouth ground glass stopper bottles, 250 ± 1 mL). 1 mL of the 2 mol/L $MnSO_4$ solution and 1 mL of the alkali-KI solution were added to the water sample. Oxygen reacts under alkaline conditions with Mn(II) forming manganese(III) hydroxide. The solution is then acidified by 1 mL of 18 mol/L H_2SO_4. Under acidic conditions Mn(III) oxidize iodide to iodine, which eventually forms I_3^- ions with the excess of KI. Let the water sample stand for 5 min in the dark. Then appropriate volume of the I_3^- solution was sampled for the measure the dissolved oxygen with the proposed I_3^--MG-PVA resonance rayleigh scattering method.

Determination of the dissoved oxygen: Appropriate volumes of the iodate standard solution (or the water sample after preparation) in the iodate concentration range were placed in a series of 10 mL colour comparison tube equipped with plug, treated with 1 mL 0.2 mol/L KI, 1 mL pH = 2.2 clacklubs solution, 1 mL 0.05 mol/L $MnSO_4$ (during preparation of the water samples, 2 mol/L $MnSO_4$ was added to react with oxygen forming manganese(III) hydroxide, so Mn(II) must be considered firstly in the spectrophotometric method). 1 mL 2×10^{-4} mol/L malachite green and 1 mL 10 g/L polyvinyl alcohol solution. The solution allowed to stand for 20 min at room temperature then completed to volume with distilled water. The resonance rayleigh scattering intensity was measured at 474 nm against a reagent blank. The working curve of iodate or dissolved oxygen could be obtained on the base of the resonance rayleigh scattering intensity corresponding to iodate concentration.

RESULTS AND DISCUSSION

Absorption spectra: Fig. 1 showed the absorption spectra of I_3^--MG-PVA complex from 350 to 800 nm. It could be seen from Fig. 1, that I_3^- had no absorption band from 500 to 800 nm. The absorption peaks of malachite green solution appeared at 420 and 620 nm. However, after I_3^- was added to the malachite green solution, the absorption peaks at 420 and 620 nm decreased with an increase in I_3^- concentration. A new absorption peak appeared at 670 nm. The new peaks at 670 nm indicated an obvious interaction between I_3^- and malachite green.
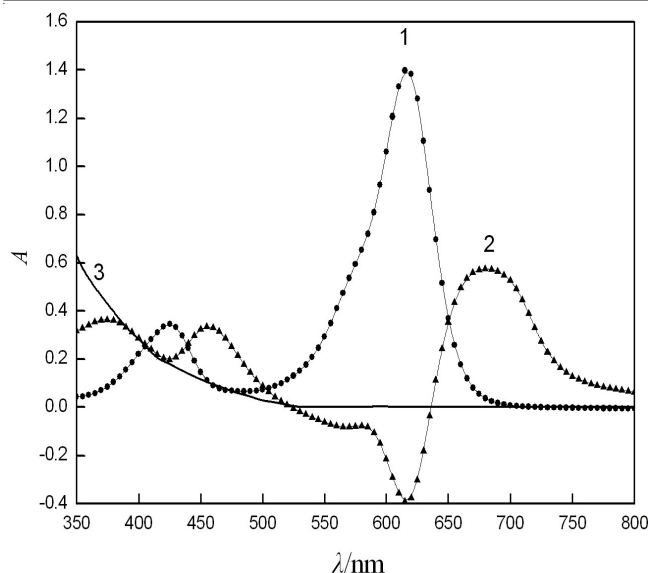
Fig. 1. Absorption spectra of the I_3^--MG-PVA system; 1. Absorption spectra of MG (against water) 2. Absorption spectra of I_3^- (against water) 3. Absorption spectra of I_3^--MG-PVA system. MG: 2×10^{-5} mol/L; I_3^- : 1.0 mg/L; PVA: 1 g/L

Resonance rayleigh scattering spectra: The resonance rayleigh scattering spectra of the I_3^--MG-PVA system were recorded by synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (Fig. 2). It could be seen that: (1) the resonance rayleigh scattering intensity of I_3^- and malachite green solution were very weak. (2)when the I_3^- reacted with malachite green to form an associated complex in the polyvinyl alcohol solution, the resonance rayleigh scattering intensity of the solution can be greatly enhanced and a new resonance rayleigh scattering spectrum appears. The maximum scattering peak is at 474 nm and there is a smaller resonance rayleigh scattering peaks at 342, 401 for I_3^--MG-PVA solution. The resonance rayleigh scattering intensities at 474 nm was increased with the increase in I_3^- concentration. So the maximum scattering wavelength, λ_{max}, is at 474 nm.
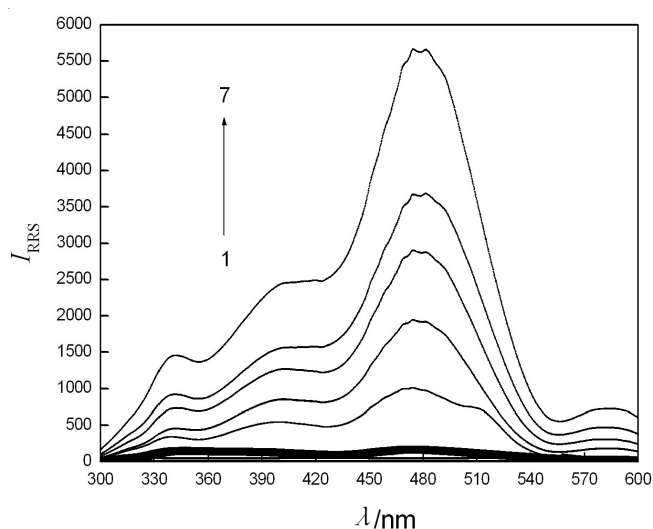

Fig. 2. Resonance rayleigh scattering spectra of the I_3^--MG-PVA system; 1. MG (2×10^{-5} mol/L) (against water blank); 2. I_3^- (1.2 mg/L) (against water blank); 3-7: I_3^--MG-PVA system(against reagent blank); concentration of I_3^-: 0.6 mg/L, 1.2 mg/L, 2.0 mg/L, 2.5 mg/L, 4.2 mg/L; concentration of MG : 2.0×10^{-5} mol/L

Effect of the surfactants: The effect of sufactants on the reaction was detected. Although the resonance rayleigh scattering intensity of the I_3^--MG complex was also strong at 474 nm without adding any surfactant solutions, the stability of the I_3^--MG complex was poor. Because the positive electric charge of malachite green was neutralized by the I_3^-, the complexes showed a hydrophobicity and mutual gathered through hydrophobic force. As time went on the precipitation of the I_3^--MG complex was generated and caused the instability of resonance rayleigh scattering. When 1 mL of 10 g/L polyvinyl alcohol was added to the I_3^--MG solution, the associated particles were more dispersed and formation of the precipitation were prevented. Meanwhile the stability and the intensity of resonance rayleigh scattering was enhanced. Experiments are also studied other surfactants on this system. Effect of type of other surfactants on spectra and sensitivity were examined and results displayed in Table-1. The results showed that the higher sensitivity in the polyvinyl alcohol than in other surfactant solutions when the same concentration of the iodate standard solution was added. So polyvinyl alcohol was selected for further studies.

TABLE-1
EFFECT OF THE SURFACTANT ON THE I_3^--MG SYSTEM

Surfactant	Without surfactant	PVA	AG	Tween 60	SDS	CTMAB
I_{RRS}	1004	1204	371.7	116.4	Precipitation	Precipitation

Effects of acidity: The pH primarily affects the degree of ionization of the malachite green and the species of I_3^-. Under the acidic condition, one N atom in the malachite green molecules is positively charged and the other neutral N atoms could be also positively charged by proton change. Therefore, an ion associated complex was formed between the malachite green and I_3^- through electrostatic attraction. Because charged hydrophilic groups been neutralized by the I_3^-, the complexes showed a hydrophobicity and mutual gathered through hydrophobic force. As long as the concentration of the malachite green and I_3^- was in certain range, this complex could not generate precipitation in the polyvinyl alcohol solution. It retained in solution with nanoparticles form and resonated rayleigh scattering.

The effects of acidity including CH_3COOH-CH_3COONa buffer solution, Clark-lubs buffer solution and Britton-Robinson (BR) buffer solution were investigated. The results showed that Clark-lubs buffer solution was better than other buffer solutions and the pH ranges of the systems were studied from 1 to 5 (Fig. 3). It was obtained by keeping the I_3^- and the malachite green concentrations constant and changing the pH. Fig. 4 showed the dependence of I_{RRS} of the I_3^--MG-PVA system on the pH of the solution. It could be seen that when the pH value was less than 2.2, the resonance rayleigh scattering intensity of the I_3^--MG-PVA complex was decreased. When the pH was above 2.2, the resonance rayleigh scattering intensity of the I_3^--MG-PVA complex also weakened and gradually decreased until the pH was less than 4.5. Then the resonance rayleigh scattering intensity of the complex decreased rapidly. Therefore, the optimum pH of 2.20 was selected for further studies.
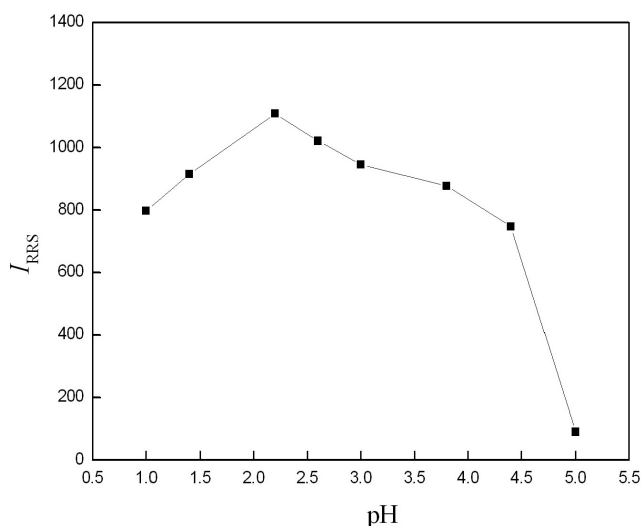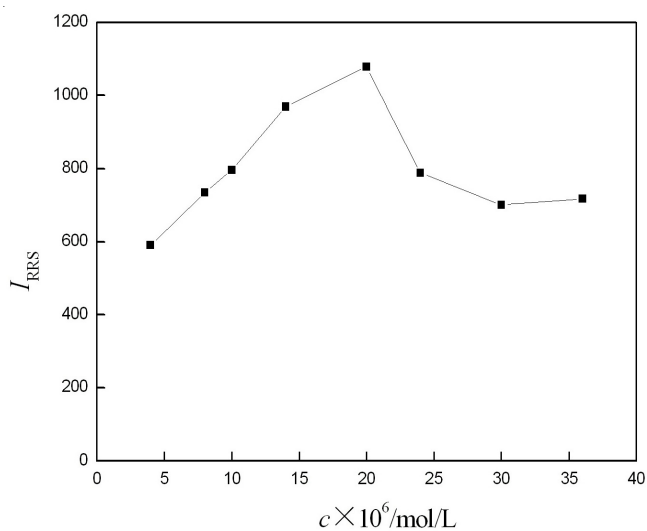
Fig. 3. Effect of pH

Fig. 4. Effect of the malachite green concentration

Malachite green could be protonated at the acidic medium and be deprotonated at a higher pH. Consequently, this cationic dye molecules has a high positive charge density at lower pH and has a low positive charge density in high pH. Thus although malachite green was better protonated in the higher acidity (pH < 1.0), I_3^- was existed as H(I_3) species mostly in this acidity. It made the I_3^- reacted with malachite green was decreased and the less I_3^- -MG-PVA complex were yielded. Thus the resonance rayleigh scattering intensity of the I_3^--MG-PVA complex was decreased. when the pH > 5, the lower positive charge density caused by the deprotonation of the malachite green also made the less I_3^--MG-PVA complex formed though I_3^- existed as the I_3^- mostly. Therefore the resonance rayleigh scattering intensity of the I_3^--MG-PVA complex was also decreased at a higher pH.

Effect of the malachite green concentration: The optimization curve for the concentration of the malachite green was shown in Fig. 4, which was obtained by keeping the I_3^- concentration and the pH constant and changing the malachite green concentration. As the malachite green concentration increased, the resonance rayleigh scattering intensity of the system increased when the malachite green concentration was less

than 2×10^{-5} mol/L and decreased when the malachite green concentration was greater than 2.0×10^{-5} mol/L. Therefore, 2×10^{-5} mol/L malachite green was selected as the optimum concentration for the determination of dissolved oxygen.

Effect of the KI concentration: The effect of the KI concentration on the scattering intensities was investigated. The result was shown in Fig. 5. As the KI concentration increased, the resonance rayleigh scattering intensity of the system increased when the KI concentration was less than 0.02 mol/L and it kept stable at the KI concentration range of 0.02-0.04 mol/L, then decreased when the KI concentration was greater than 0.04 mol/L. Therefore 0.03 mol/L KI was selected as the optimum concentration for determnation of dissolved oxygen. when the KI concentration was less than 0.02 mol/L, the incompletion of the interaction of I_3^- and malachite green lead to the resonance rayleigh scattering intensity of I_3^--MG-PVA system weak. When the KI concentration was higher than the optimum concentration, excessive I^- reacted with malachite green cations to form an associated complex, resulting in the resonance rayleigh scattering intensity of the I_3^--MG-PVA system decrease.
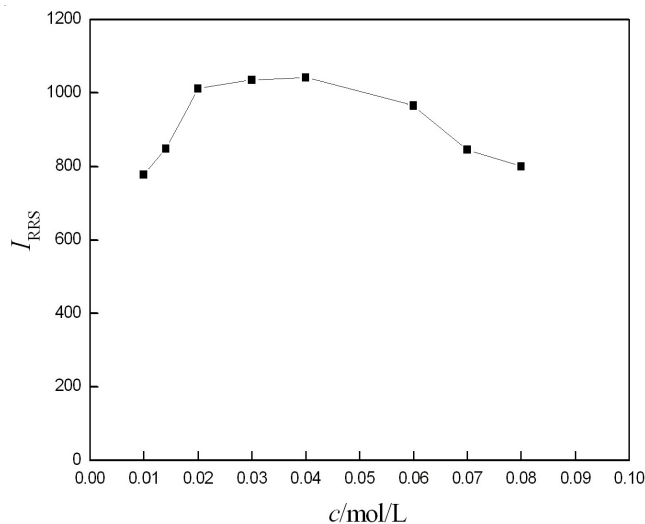

Fig. 5. Effect of the KI concentration

Effect of reaction time: The effect of reaction time on the scattering intensities was investigated. The results showed that the enhancement of intensities of scattering (I_{RRS}) were reached the maximum after 10 min and could be kept steadily for 40 min under room temperature and then decreased gradually. So 20 min was recommended for the further study.

Effect of interfering ions: Under the recommended conditions, the effects of various foreign ions on the determination of 2.74 mg/L of dissolved oxygen were measured. The interference of foreign substrates were discussed with a relative error of less than ± 5 %, the tolerance limits for various foreign ions were as follows: F^-(1500), NH_4^+, Na^+, Zn^{2+}, K^+, Ca^{2+}, Mg^{2+} (1000), Fe^{2+}, Al^{3+}, HPO_4^{2-}, $H_2PO_4^-$, Cl^- (300), Ni^{2+}, Ba^{2+}(100), Fe^{3+}(2). It was showed that most of the metal ions did not influence the determination of dissolved oxygen. Generally speaking, because the content of Fe^{3+} is negligible in the water when compared with the amount of dissolved oxygen, so the effect on the colour reaction caused by Fe^{3+} could be neglected. If NO_2^- were found in the water

sample and its contents were more than 0.1 mg/L, the excessive dissolved oxygen would obtained because extra I_2 were formed from the reaction between NO_2^- and KI. In order to eliminate the interference a few drops of 50 g/L NaN_3 could be add to the water sample before the precipitation were dissolved by H_2SO_4.

Calibration, linear ranges and detection limits: Under the optimum conditions, the I_{RRS} values of the I_3^--MG-PVA complexes were measured at their maximum scatter wavelength and calibration graphs of I_{RRS} against concentration of dissolved oxygen were constructed. The correlation parameters are presented in Table-2. It is found that I_{RRS} is directly proportional to the concentration of dissolved oxygen in a certain range. The detection limits (DL) of the systems, which were calculated as three times the standard deviation for the blank buffer solution were also listed in the Table-2.

TABLE-2
PARAMETERS OF ANALYSIS

Parameters of analysis	The proposed method
LR of DO (mg/L)	0.2-3.0
The regression equation	$I_{RRS} = 251.4 + 1299.7\,\rho_{O_2}$ (mg/L)
Correlation coefficient	0.9939
LOD of DO (mg/L, S/N = 3)	0.025
S.D. (%)	0.02
LR, Linear range; LOD, detection limit (defined on the basis of three times the standard deviation of the blank)	

Water sample analysis: Collect the water samples from the river, distilled, seawater and the Sewage treatment plants, then the dissolved oxygen in the water sample was converted to iodine complex. The amount of dissolved oxygen (mg/L) in the water sample was determined by the proposed resonance rayleigh scattering method. The Winkler's method was also used to determine the dissolved oxygen in the same sample at 20 ℃. The results were shown in Table-3. Averages and variances of the differences between the two methods were homogenous (T-test and student's test at the 95 % confidence level). Furthermore, 20 samples were analyzed in 40 min by spectrophotometry instead of 1-2 h by titration.

TABLE-3
CONCENTRATION OF DISSOLVED OXYGEN OF DIFFERENT SAMPLE (95 % CONFIDENCE)

Sample (℃)	Proposed method (n = 10) (mg/L)	Winkler method (n = 6) (mg/L)
Distilled water (20 ℃)	11.04 ± 0.03	10.95 ± 0.03
Seawater (20 ℃)	7.82 ± 0.04	7.75 ± 0.02
Water in domestic school at 6:00 pm (10 ℃)	10. 69 ± 0.05	10. 58 ± 0.02
Water in domestic school at 5:00 pm (10 ℃)	12.05 ± 0.04	11. 87 ± 0.02
Sewage (10 ℃)	9. 10 ± 0.03	9. 04 ± 0.04

Conclusion

Dissolved oxygen is one of the most important substance present in water. Dissolved oxygen is central in studies on biological productivity and biochemical processes in the aquatic environments. For these reasons, an increasing amount of attention has been paid to the determination of dissolved oxygen. In this paper, we have developed a novel method for the determination of trace amounts of dissolved oxygen based on the formation of an I_3^--MG-PVA complex by resonance rayleigh scattering. Compared with the Winkler method the more stable solution in our research work was used and less frequent calibration was required in the proposed resonance rayleigh scattering method. All the solutions of the reagents used could be kept stable for longer time. The water sample after pretreatment were only taken less than 2 mL. Because of using photometric method instead of traditional redox titration method, therefore, the changes in oxygen concentrations of less than 1 mg/L and the volatilization of iodine and the oxygen dissolved in the reagents used could also be ignored in the spectrophotometric method. Furthermore, a complete analysis could be performed in 0.5 h including pretreatment and detection, giving a very high throughput of 20 samples in about 40 min. It is suggested as being a suitable alternative to titration in most applications of the Winkler determination of dissolved oxygen. Furthermore, we successfully apply the resonance rayleigh scattering method to the analysis of the dissolved oxygen in real enviromental samples. This phenomenon further enlarges the study and application range of the resonance rayleigh scattering method and provides new information for study based on resonance rayleigh scattering.

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