

# Determination of Lead (II) in environmental water samples by resonance light scattering technology

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**Abstract.** Lead is a heavy metal with neurotoxicity, and excessive lead in water can lead to the deterioration of water quality and accumulate in aquatic organisms. Thus, it is necessary to explore quick and effective methods for the determination of Pb<sup>2+</sup> in water environment. In pH=5.5 weak acidic solution, it is found that Pb<sup>2+</sup> can combine with XO to form a red complex PbXO, which has a strong resonance light scattering strength at the wavelength of 342 nm under the sensitization effect of the cetyl trimethyl ammonium bromide(CTMAB). The resonance light scattering strength has good linear relationship with the concentration of Pb<sup>2+</sup> in the range of 0.01 mg L<sup>-1</sup>~0.1 mg L<sup>-1</sup>. Therefore, a convenient strategy has successfully realized the lead detection with the detection limits of 1.05×10<sup>-2</sup> mg L<sup>-1</sup> and the relative standard deviation of 1.89 % at a concentration 0.02 mg L<sup>-1</sup>. The recovery is in the range of 88.3%~98.3% for the determination of Pb<sup>2+</sup> in three different water samples. It is used for the determination of Pb<sup>2+</sup> in water samples with satisfactory results.

## 1. Introduction

Heavy metals pollution is of great environmental concern, due to the extreme destructiveness and extensive influences. Among them, lead is one of important target because of its ubiquity and effect on human being.<sup>[1-4]</sup> Lead poisoning can cause memory loss, irritability, anemia, muscle paralysis and mental retardation.<sup>[5-6]</sup> Especially for the children, it can cause severe brain damage, resulting in insufficient attention and learning disabilities.<sup>[7]</sup> Although some countries have introduced a series of policies to deal with this issue, but the practical effects are still far from satisfied.<sup>[8]</sup> Therefore, it is necessary and critically important to determine lead by simple and efficient method.

Many analytical techniques have been applied for the determination of lead, including atomic absorption spectrometry (AAS)<sup>[9-10]</sup>, atomic emission spectrometry (AES)<sup>[11-12]</sup>, spectrophotometry<sup>[13]</sup> and so on. Among them, atomic absorption spectrophotometry is used as national standard methods of China, which has the advantages of simplicity, rapid, accuracy and high sensitivity. In general, lead ions are present in trace amounts in aqueous environments and therefore must be extracted before detection. However, the extraction process for many detection methods is complex. Accordingly, developing of simple and rapid determination methods of Pb<sup>2+</sup> is indispensable.

Recently, resonance light scattering (RLS) has been increasingly applied to the study and determination of some biological macromolecules, organic substances, inorganic ions, etc.<sup>[14-18]</sup> Compared with other analytical methods, RLS has the distinct advantages of being less time-consuming, requiring only simple instrumentation, and having high sensitivity. Furthermore, it can be accomplished with a common fluorescence spectrometer and using inexpensive and safe reagents.



In the present work, it is found that  $\text{Pb}^{2+}$  reacted with xylenol orange (XO) to form a red complex  $\text{PbXO}$  in buffer solution of  $\text{pH} = 5.5$ , and due to the sensitization effect of CTMAB, the resonance light scattering intensity of system is enhanced. So a new method of resonant light scattering with good stability and sensitivity and rapid detection of  $\text{Pb}^{2+}$  has been established. The method is simple to operate, has a wide range of applications and high sensitivity. Compared with the current national standard method for detection of  $\text{Pb}^{2+}$ , the method does not require digestion, and the method is simpler and more sensitive, relatively inexpensive in terms of the analytical instrument price, with good application prospects.

## 2. Experimental

### 2.1. Apparatus and reagents

All the RLS spectra were measured on a RF-5301 fluorescence spectrofluorometer (Shimadzu Company, Japan). A UV-Vis 2550 spectrophotometer (Shimadzu Company, Japan) was used for recording the absorption spectra. Seman GGX-6 Flame Atomic Absorption Spectrophotometer (FAAS) (Beijing Kechuang Haiguang Instrument Co., Ltd.) was used to determine the concentration of  $\text{Pb}^{2+}$  in real water samples. A PHS-3C acidity meter (Shanghai Precision & Scientific Instrument Co. Ltd., Shanghai) was used for adjusting pH values.

$\text{Pb}^{2+}$  standard solution was purchased from National steel material test center, China, analytical reagent grade. The concentration of  $\text{Pb}^{2+}$  stock solution was  $1.0 \text{ mg mL}^{-1}$  and the working solution was prepared by diluting the stock solution to  $1.0 \mu\text{g mL}^{-1}$ . Xylenol orange (XO, Chengdu Kelong Chemical Reagent plant, China): the concentration of XO solution was  $1 \times 10^{-3} \text{ mol L}^{-1}$ . Cetyl trimethyl ammonium bromide (CTMAB) (Chengdu Kelong Chemical Reagent plant, China): the concentration of CTMAB solution was  $1 \times 10^{-3} \text{ mol L}^{-1}$ . Hexamethylenetetramine used as buffer solutions and the pH values were adjusted by pH acidity meter. All reagents were analytical reagent grade and the milli-Q ultrapure water was used throughout unless it is specified.

### 2.2. General procedure

According to the experimental order, suitable amount of  $\text{Pb}^{2+}$  working solution, 2 mL hexamethylenetetramine buffer ( $\text{pH} = 5.5$ ), 0.3 mL of xylenol orange aqueous solution (0.1%) and 2 mL of CTMAB ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) were sequentially added into a 10 mL colorimetric tube. The resulting solution was diluted to the mark with water and mixed thoroughly, then it was set aside for 20 min. RLS spectra of the system were recorded with synchronous scanning at  $\lambda_{\text{ex}} = \lambda_{\text{em}}$  with 10 nm of excitation and emission-slit widths, and RLS intensity ( $I_{\text{RLS}}$ ) for sample solution and  $I_{\text{RLS}}^0$  for reagent blank were measured at 342 nm,  $\Delta I_{\text{RLS}} = I_{\text{RLS}} - I_{\text{RLS}}^0$ .

## 3. Results and discussion

### 3.1. Resonance light spectra

The RLS spectra of different mixed solutions are shown in figure 1, according to the abovementioned experimental procedure. From figure 1, it can be seen that the RLS intensities of single  $\text{Pb}^{2+}$ , XO and CTMAB are relatively weak. The same phenomena obtained when mixed  $\text{Pb}^{2+}$ , XO and CTMAB each other. But when  $\text{Pb}^{2+}$  is reacted with XO to form a red complex  $\text{PbXO}$  and sensitized by CTMAB, the RLS spectra are enhanced greatly with scattering peaks at 342 nm. Therefore, 342 nm was chosen as the measuring wavelength.

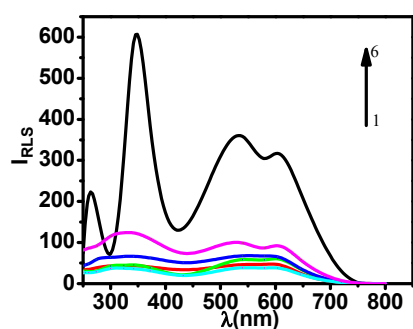


Figure 1. Resonance light spectra of different mixed systems. 1: CTMAB 2:  $\text{Pb}^{2+}$  3: XO 4:  $\text{Pb}^{2+}$ -CTMAB 5: Pb 6:  $\text{Pb}^{2+}$ -XO-CTMAB.

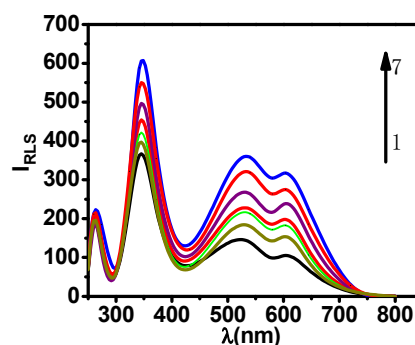


Figure 2. Resonance light spectra of  $\text{Pb}^{2+}$ -XO-CTMAB system. 1: blank; 2-7  $\text{Pb}^{2+}$ -XO-CTMAB; C ( $\text{Pb}^{2+}$ ): 0.01, 0.02, 0.04, 0.06, 0.08 and  $0.1 \text{ mg L}^{-1}$ .

The RLS spectra of  $\text{Pb}^{2+}$ -XO-CTMAB system are shown in figure 2, it can be seen that the resonance light scattering intensity of XO and CTMAB is the lowest when there is free of  $\text{Pb}^{2+}$  in the solution system. But when  $\text{Pb}^{2+}$  is reacted with XO to form a red complex  $\text{PbXO}$ , the RLS spectra are enhanced greatly. Meanwhile, there is a better linear relationship with the concentration of  $\text{Pb}^{2+}$  and resonance light scattering intensity, which can be applied to the determination of  $\text{Pb}^{2+}$ .

### 3.2. Optimum reaction conditions

#### 3.2.1. Effect of hexamethylenetetramine buffer solution concentration.

Various kinds of acid and buffer solutions such as NaAc-HAc buffer solution, BR buffer solution, hydrochloric acid, hexamethylenetetramine buffer solution were used to investigate the effects of acidity on the RLS strength. The results indicate that hexamethylenetetramine buffer solution is the best.

When hexamethylenetetramine buffer solution was used as the reaction medium, different volume of hexamethylenetetramine buffer solution was tested. The results are shown in figure 3, they suggest that 2.0 mL dosage of hexamethylenetetramine buffer solution is the best. At the range of 1.6 mL ~ 2.0 mL, the scattering light intensity increased stably with the increasing of volume, and after 2.0 mL tends to be stable, so 2.0 mL hexamethylenetetramine buffer was chosen.

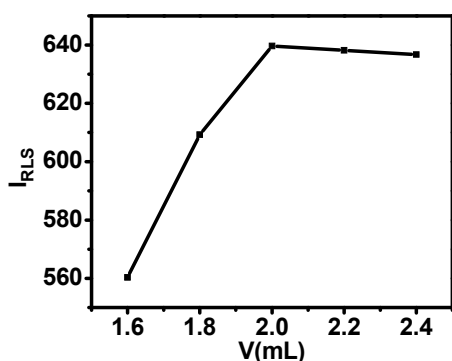


Figure 3. Effect of hexamethylenetetramine buffer solution dosage on RLS intensity.

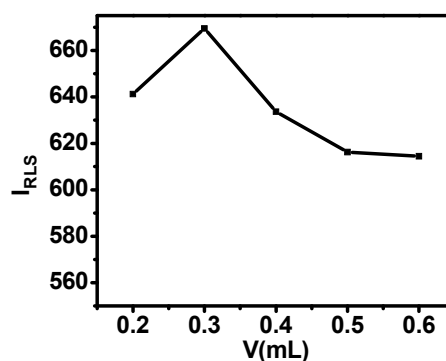


Figure 4. Effect of xylenol orange dosage on RLS intensity.

### 3.2.2. Effect of xylenol orange concentration.

Under the selected experimental conditions, the influence of the volume of xylenol orange on the RLS intensity of the system was detected. As shown in figure 4, it is indicate that 0.3 mL dosage of xylenol orange is appropriate. When the dosage of xylenol orange was lower or higher than 0.3mL,  $\Delta I_{\text{RLS}}$  decreased obviously. Consequently, the selection of 0.1% xylenol orange solution volume is considered to be 0.3mL.

### 3.2.3. Effect of CTMAB solution concentration.

At the same time, effects of many kinds of surfactants such as polyvinyl alcohol (PVA), tween-20, cetyl trimethyl ammonium bromide (CTMAB) on the RLS intensity were inspected. It is found that the CTMAB works well for the system. It can be seen from figure 5, the RLS intensity increased steadily when the added volume of CTMAB is in the range of 1.4-2.0 mL. But when the added volume is higher than 2.0 mL, the RLS intensity continually decreased. Hence, 2.0 mL of CTMAB ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) was selected in the further experiments.

### 3.2.4. Effect of ionic strength.

The effects of different concentrations of NaCl solution on the resonance light scattering were also investigated. The results are shown in figure 6. From figure 6, the RLS intensity of the system decreased with the increase of NaCl concentration. The reason is maybe the excess NaCl produced electrostatic shielding effects, which block the reaction and combination of  $\text{Pb}^{2+}$  with xylenol orange. Accordingly, all the experiments do not need to add NaCl to control the intensity of ions.

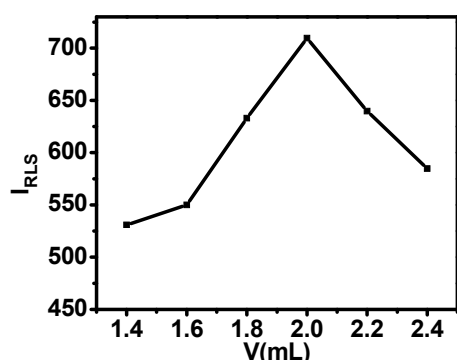


Figure 5. Effect of CTMAB solution dosage on RLS intensity.

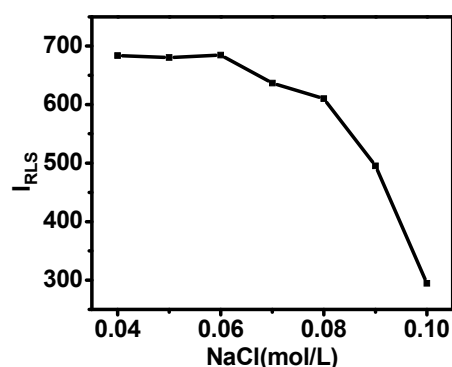


Figure 6. Effect of ionic strength on RLS intensity.

### 3.2.5. Other influence factors.

After fixing the experimental conditions, different order of addition of  $\text{Pb}^{2+}$  working solution, xylenol orange solution, CTMAB solution and hexamethylenetetramine buffer solution were investigated. It was found that there is not much impact on the system's resonance light scattering intensity. And the influences of temperature on the RLS intensity between 20 °C to 60 °C were tested respectively. The results showed that the resonance light scattering intensity tends to be stable within the range of 20 °C ~ 60 °C. Therefore, room temperature were selected in the following experiments.

### 3.2.6. Reaction speed and the stability of scattering system.

According to the experimental method, certain amount of  $\text{Pb}^{2+}$  working solution, 0.3mL of xylenol orange aqueous solution (0.1%), 2mL of hexamethylenetetramine buffer solution (pH = 5.5) and 2mL of cetyl trimethyl ammonium bromide ( $1 \times 10^{-2} \text{ mol L}^{-1}$ ) were added into a 10 mL colorimetric tube,

respectively. Then it was diluted to the mark and vibrated thoroughly. The measurement of RLS signal was carried out every 5 min (from 0 min to 40 min). The result indicated that the system can completely react within 20 min and remains stable for a long period of time. So the reaction time of experiment selection is 20 min.

### 3.3 Analytical merits of methods

Under optimized experimental conditions, different concentrations of  $\text{Pb}^{2+}$  working solution were applied to the determination of  $I_{\text{RLS}}$  in view of the system. When the concentration of  $\text{Pb}^{2+}$  is in the range of  $0.01 \text{ mg L}^{-1}$  to  $0.1 \text{ mg L}^{-1}$ , the intensity of the resonance scattered light has a good linear relationship with the concentration of  $\text{Pb}^{2+}$ . The linear regression equation is  $y = 2009.97C + 9.27$ ,  $R^2 = 0.9933$ . The detection limit of the method is  $1.05 \times 10^{-2} \text{ mg L}^{-1}$ , which was calculated according to the regulation of IUPAC.

### 3.4 Effect of coexistent substances

Effects of 14 kinds of coexisting substances on the system were studied. While the content of  $\text{Pb}^{2+}$  was  $200 \mu\text{g L}^{-1}$ , most common ions did not interfere with the determination of  $\text{Pb}^{2+}$ . Such as  $\text{Zn}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{W}^{6+}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Mg}^{2+}$  and  $\text{NO}_3^-$ , their coexistence multiple were greater than or equal to 200 times of  $\text{Pb}^{2+}$ . And that of  $\text{Hg}^{2+}$ ,  $\text{Cr}^{2+}$ ,  $\text{Ag}^+$  and  $\text{Cd}^{2+}$  were 20, 50, 20 times and 50 times, respectively. But there were bigger interferences of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$  and  $\text{Cu}^{2+}$  for the determination of  $\text{Pb}^{2+}$ . In the determination of water samples,  $\text{Fe}^{3+}$  did not interfere with the determination when added NaF as a masking agent. When EDTA was added as a masking agent,  $\text{Al}^{3+}$  did not interfere with the determination. When  $\text{SCN}^-$  was used as a masking agent,  $\text{Cu}^{2+}$  did not interfere with the determination. Relatively, the method has good selectivity.

### 3.5 Analytical application

Detection of trace  $\text{Pb}^{2+}$  in water samples using RLS methods were listed in table 1. As a control method, FAAS determination of  $\text{Pb}^{2+}$  in the same water sample was also carried out. The results showed that the recoveries of the method are between 88.3% and 98.3%, the relative standard deviation (RSD) is between 1.75% and 4.34%. And there is no significantly difference between these two methods for the same samples. It demonstrated that this method can quickly and accurately determine the trace amount of lead ion in real water samples.

Table 1. Determination results of  $\text{Pb}^{2+}$  in water samples (n=3)

Samples	Method	Founded ( $\text{mg L}^{-1}$ )	Added ( $\text{mg L}^{-1}$ )	Measured ( $\text{mg L}^{-1}$ )	Recovery (%, n=3)	RSD (%, n=3)
Tap water	RLS	n.d	0.060	0.058	93.3~96.7	1.75
				0.056		
	AAS	n.d	0.100	0.057	90.1~93.7	1.96
				0.0937		
mineral water	RLS	n.d	0.060	0.0919	88.3~95.0	4.34
				0.0901		
	AAS	n.d	0.100	0.053	89.3~93.4	2.51
				0.057		
Huaihai Lake water	RLS	0.016	0.060	0.053	90.0~98.3	3.67
				0.0934		
	AAS	0.013	0.100	0.0924	89.8~96.5	3.34
				0.0893		

0.1028

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n.d: not detected

#### 4. Conclusion

In the presence of weak acid buffer,  $\text{Pb}^{2+}$  reacted with xylenol orange (XO) to form a red complex  $\text{PbXO}$ , and due to the sensitization effect of cetyl trimethyl ammonium bromide (CTMAB), the system's RLS intensity is greatly enhanced. Thus a new method for detection of  $\text{Pb}^{2+}$  in environmental water samples has been established. And the method has the advantages of simple operation, high sensitivity, fast detection speed, low price of experimental instruments and the like, it's suitable for the analysis and detection of  $\text{Pb}^{2+}$  in routine environmental water samples.

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#### References

- [1] Hsu P C and Guo Y L 2002 *Toxicology*. **180** 33-44.
- [2] Kang W J, Pei X, Rusinek C A, Bange A, Haynes E N, Heineman W R and Papautsky I 2017 *Anal. Chem.* **89** 3345
- [3] Qiu G, Ng S P, Liang X, Ding N, Chen X, and Wu C L 2017 *Anal. Chem.* **89** 1985-93
- [4] Arduini F, Calvo J Q, Amine A, Palleschi G and Moscone D 2010 *Trac Trends in Analytical Chemistry*. **29** 1295-304
- [5] Chen T C and Huang W P 2002 *Journal of the American Chemical Society*. **124** 6246-7
- [6] Morales K A, Lasagna M, Gribenko A V, Yoon Y, Reinhart G D, Lee J C, Cho W, Li P and Igumenova T I 2011 *Journal of the American Chemical Society*. **133** 10599-611
- [7] Huang Y S, Ma Y L, Chen Y H, Wu X M, Fang L T, Zhu Z and Yang C J 2014 *Anal. Chem.* **86** 11434-9
- [8] Ali E M, Zheng Y, Yu H H and Ying J Y 2007 *Anal. Chem.* **79** 9452-58
- [9] Tan Q, Wu P, Wu L and Hou X 2006 *Microchimica Acta*. **155** 441-5
- [10] Correia P R M, Oliveira E and Oliveira P V 2000 *Analytica Chimica Acta*. **405** 205-11
- [11] Gazieva M T, Pometun E A and Pachadzhannov D N 2006 *Journal of Analytical Chemistry*. **61** 273-8
- [12] Zhang J 2005 *Modern Instruments*. **5** 26-33
- [13] Khan H, Ahmed M J and Bhanger M I 2015 *Spectroscopy*. **20** 285-97
- [14] Xiang H, Xie Y and Huang J 2011 *Journal of Analytical Chemistry*. **66** 618-22
- [15] Zhang B, Liu H, Huang X, Dong C and Ren J 2017 *Anal. Chem.* **89** 12609-16
- [16] He Y, Liao L, Xu C, Wu R, Li S and Yang Y 2015 *Microchimica Acta*. **182** 419-26
- [17] Wang C, Wang C, Wang Q and Chen D 2017 *Analytical & Bioanalytical Chemistry*. **409** 1-8
- [18] Li T, Liu D and Wang Z 2010 *Anal. Chem.* **82** 3067-72