Determination of Trace lead (Ⅱ) by Resonance Light Scattering Based on Pb (Ⅱ)-KI-MG System

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Abstract. In pH=3.0 weak acidic solution, it is found that Pb^{2+} can react with I^- to form $[PbI_4]^{2-}$, and it further reacted with MG to form ion-association complex. As a result, the new spectra of RLS appeared and their intensities enhanced greatly. Accordingly, a new method developed for the determination of Pb (II).The appropriate reaction conditions were optimized through experiments. The results show that a strong and stable resonance scattering spectra emerge at the wavelength of 338 nm. The resonance light scattering strength (ΔI_{RLS}) has good linear relationship with the concentration of Pb (II) in the range of 0.2 μg/mL ~ 1.0 μg/mL. The detection limits (LOD) is 0.0155 μg/mL. The relative standard deviation (RSD) is 3.61% (n=11) for the determination of 0.6 μg/mL Pb (II) standard solution. And this method was successfully applied to the determination of three environmental water samples (nongfu spring, tap water, laboratory wastewater). Results illustrate that the addition standard recovery are 80%~107% with relative standard deviation (RSD) between 1.8% to 4.6%.

1. Introduction

As a strong neurotoxin heavy metal element, lead has been considered as one of the most serious environmental pollutants in human civilization. Lead is widely used in many fields, such as industry and transportation, and lead pollution in living environment seriously endangers human health. [1] According to relevant medical report, children's blood lead levels above or equal to 100 g/L will have an effect on children's intellectual development, leading to a decline in children's intelligence. The blood lead content of children was significantly negatively correlated with IQ (IQ). When blood Pb (II) levels increased by 100 g/L, the average IQ decreased by 1~3 points. Thus, the detection of Pb (II) content, especially in environmental water samples, remains a key challenge in the implementation of environment measuring and controlling. [2]

At present, the methods of determination of Pb (II) include atomic absorption spectrometry (AAS), [3-6] spectrophotometry [7-10] and paleography [11-13]. Among them, the AAS is fast and accurate, but the Pb(II) content in the water is usually low, and the detection limit of this method can hardly meet the requirements of trace analysis. On the other hand, such samples must be preseparated and enriched before used. Spectrophotometry is one of effective detection methods that can realize simultaneous detection of large samples, while the low degree of accuracy limits its practical application. In addition, paleography is another convenient method, but suffers from its large errors. Therefore, the development of simple and rapid determination methods of Pb (II) with high detection limit and accuracy are crucial. The determination of Pb (II) by RRS is a new method, which have the advantages of higher sensitivity, simplicity and easy operation. It has been widely used to the research of biological macromolecule, pharmaceuticals, nanoparticals, surfactants, metal and non-metal ions in the environmental samples.[14,15] Compared with the traditional method, such RRS, has the

characteristics of using nontoxic substances, saving reagents and samples, and its operation is simple and easy.

In this work, We investigate pH = 3, Pb(II) with too much I^- ions form $[PbI_4]^{2-}$ complex anion, and further form ion association with MG, so that the system of the resonance light scattering intensity is enhanced, thus establishing a kind of spirit high lightness, good selectivity, fast, accurate determination of Pb(II).

2. Experiment section

2.1. Apparatus and reagents

A RF-5301 spectrofluorophotometer (Shimadzu Company, Japan) was used for recording and measuring the RLS and fluorescence spectra. A UV-2550 spectrophotometer (Shimadzu Company, Japan) was used for recording the absorption spectra. A PHS-3C acidity meter (Shanghai Precision & Scientific Instrument Co. Ltd., Shanghai) was used for adjusting pH values.

The concentration of Pb (II) stock solution is 1.0 mg mL^{-1} and the working solution has been prepared by diluting the stock solution to 1.0 μg mL^{-1}.1.0×10^{-3} mol L^{-1} of malachite solution is used as stock solution, and it is diluted to 1.0×10^{-4} mol L^{-1} working solution. The stocking solution concentration of potassium iodide and hydrochloric acid are 10% (mass concentration) and 1.0×10^{-3} mol L^{-1}, respectively.

All reagents are analytical reagent grade and come from Chengdu Kelong Chemical Reagent Factory. The milli-Q ultrapure water is used throughout.

2.2. General procedure

According to the experimental order, suitable amount of Pb(II) wording solution,0.8 mL HC1 solution, 2.6mL malachite working solution, 0.6mL of potassium iodide solution(10%)were injected into a 10.0 mL calibrated glass tube. The resulting solution was diluted to the mark with ultrapure water and mixed thoroughly, and then it was set aside for 15 min before determination. The RLS spectra of the system were recorded with synchronous scanning at λ ex = λ em and RLS intensity (I_{RLS}) for sample solution and I^0_{RRS} for reagent blank at 338 nm were measured accordingly, $\Delta I_{RLS} = I_{RLS} - I^0_{RLS}$. The selected excitation and emission-slit widths are 10nm.

3. Results and discussion

3.1. RLS spectra

The RLS spectra of Pb (II)-I^--MG system are shown in Fig.3-1 and Fig.3-2. From Fig.3-1, it can be seen that the RLS intensities of single Pb (II), MG solution, and I- or the mixture solution of any two of them are very weak. However, when Pb (II), I^- and MG mixed each other, the intensities of RLS spectra are enhanced greatly due to the formation of a ternary ion association complex. And four obvious scattering peaks located at the wavelength of 338 nm, 468 nm, 589 nm and 660 nm, respectively. From Fig.3-2, the shape and stability for the peak of 338 nm are relatively good, and the added value of scattering intensities (ΔI) increase with the accretion of Pb (II) concentration. There is a good linear relationship between ΔI and Pb (II) concentration, which can be applied to the determination of Pb (II). Therefore, 338 nm was chosen as the quantitative measuring wavelength in further experiments.
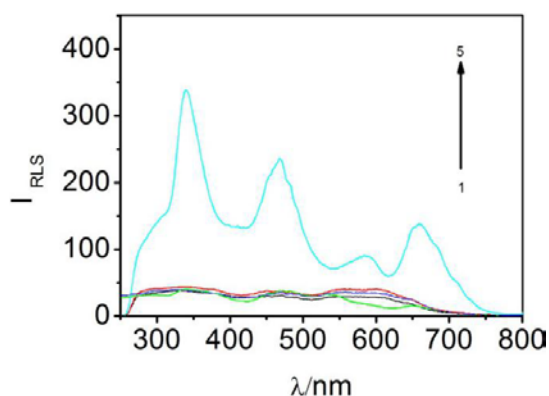
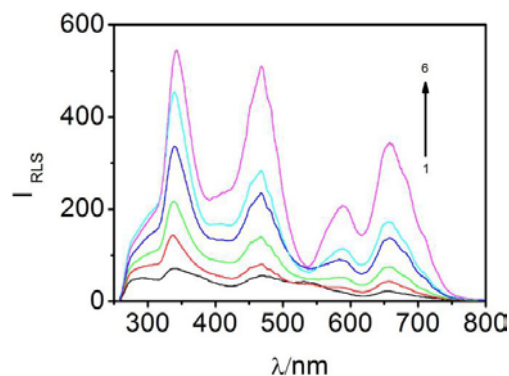**Figure.3-1.** The resonance light scattering spectra of various system.1-5:Pb

Figure.3-2. The resonance light scattering spectra of Pb(II)-I--MG reaction system.1-6(cPb2+):0.2, 0.4, 0.6, 0.8, 1.0μgmL-1; cKI:10%(mass concentration); cMG: $1.0 \times 1035 molL-1$; pH=3.0

3.2. Optimum Reaction Conditions

3.2.1. Effect of acidity. Various kinds of acid and buffer solutions, such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid, HC1-NaAc buffer solution and BR buffer solution, were used to investigate the effects of acidity on the intensity of RLS. The results indicate that 1.0×10^{-3} mol L^{-1} hydrochloric acid is the best. When hydrochloric acid was used as the reaction medium, different volume of 1.0×10^{-3} mol L^{-1} hydrochloric acid was tested. The results suggest that 0.8 mL dosage of hydrochloric acid is the best. When the addition value of hydrochloric acid was lower or higher than 0.8mL, ΔI_{RLS} decreased obviously. Thus, 1.0×10^{-3} mol L^{-1} hydrochloric acid was chosen as the reaction medium in the following experiments, and the appropriate addition amount of 0.8 mL was used in view of the strength and stability of RLS signal.
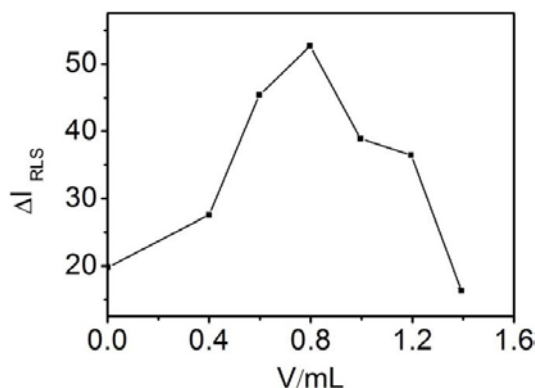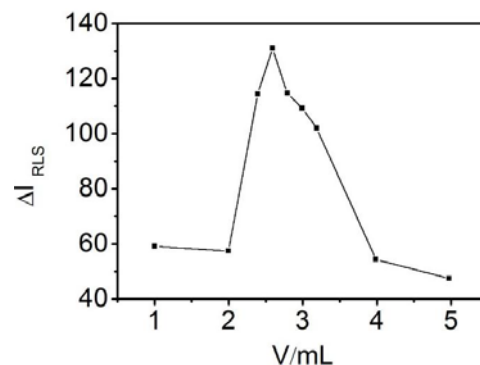

Figure.3-3. Effect of HCl dosage on ΔI_{RLS}

Figure.3-4. Effect of MG dosage on ΔI_{RLS} cPb^{2+}: 100.0μg L^{-1}; cKI: 2.8×10^{-3} mol L^{-1}; pH=3.0

3.2.2. Effect of MG concentration. Effects of MG concentration on RRS were examined. 1 to 5 mL of 1.0×10^{-4} mol/L MG solution were added into the system respectively. The influences on RLS intensity of various dosage of MG are shown in Fig.3-4. When the dosage of MG is in the range of 1 to 2.6 mL, the relatively ΔI_{RLS} intensity increased accordingly. However, when the dosage is higher than 2.6 mL, the ΔI_{RLS} intensity continually decreased. The maximum ΔI_{RLS} intensity occurred at the dosage of 2.6mL. Consequently, the addition of 1.0×10^{-4} mol/L MG was selected as 2.6 mL in the next experiments.

3.2.3. Effect of potassium iodide concentration. Generally, excessive potassium iodide is required for

fully formation of $[PbI_4]^{2-}$ from trace amount of Pb (II) with iodide. Therefore, effects of the concentration of potassium iodide on RRS intensities (ΔI_{RLS}) were tested using higher concentration (10% mass concentration) of potassium iodide. The results are shown in Fig.3-5. It is can be seen from Fig.3-5, when the addition of potassium iodide was 0.6 mL, ΔI_{RLS} reached maximum and stable. Therefore, 0.6mL of potassium iodide was chosen in the subsequent experiments.
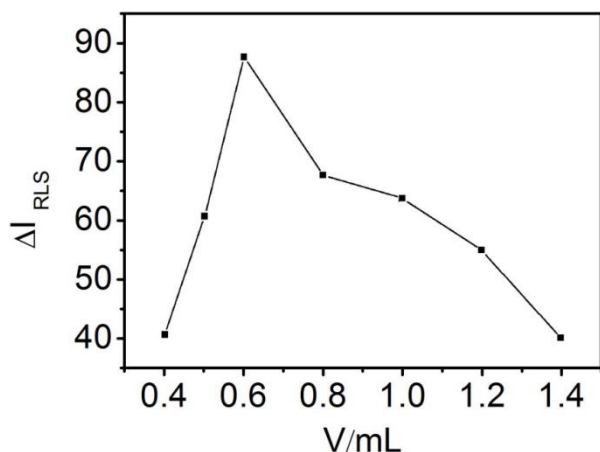

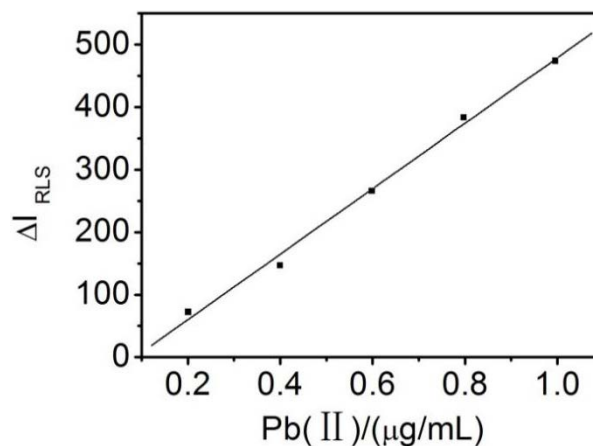**Figure.3-5.**Effect of KI dosage on ΔI_{RLS} **Figure.3-6.**Calibrate curve

3.2.4. Other influence factor. Different kinds of surfactants were inspected in this scattering system, which included arabic gum, cetylpyridinium bromide, Triton X-100, hexadecyltrimethyl ammonium bromide and laurel sodium sulfate. The results indicated that there are not influences on the system. And the influence of temperature through 10℃ to 60℃ was examined. It is no distinctive influence. Accordingly, room temperature and no surfactants were selected in the following experiments.

3.2.5. Reaction speed and the stability of scattering system. At room temperature (15-25°C), the RLS intensity (ΔI_{RLS}) reached maximum within 15 min, and it could remain constant within 70 min free from the straight irradiation of sunlight. After that, the RLS intensity (ΔI_{RLS}) gradually reduced. So the experiment should be accomplished within 70 min. normally, we performed the whole determination within 15-20min. Moreover, there is not obviously influence on the magnitude of RLS intensity (ΔI_{RLS}) of different mixing sequence of reaction reagents.

3.2.6. Effect of ionic strength. The influences of ionic strength on RLS intensity (ΔI_{RLS}) were investigated by introducing NaCl into the mixed solution. Results show that the RLS strength will decrease when the concentration of NaCl is higher than 0.05 mol L^{-1}, but there is no obvious influence on scattering strength of the system as the concentration of NaCl is lower than 0.05 mol L^{-1}. The reason is maybe the electrostatic screening effect by excessive NaCl in solution, which interfered with the combination of MG with $[PbI_4]^{2-}$. Thus, other inorganic salt should not be introduced under normal circumstances.

3.3. Sensitivity of methods
Under the selected optimum reaction conditions, the linear regression equations were performed. The specific information was displayed in Fig.3-6. It can be seen from Fig.3-6 that the intensity of ΔI_{RLS} has good linear relationships to the concentration of Pb (II) in the range of 0.2-1.0μg mL^{-1}. The correlation coefficient is 0.9986, and the detection limits is 0.016μg mL^{-1}.

3.4. Effect of coexistent substances
Effects of more than 20 kinds of coexisting substances were tested by using RLS method. While the content of Pb (II) is 200 μg L^{-1}, relative error within ±5%, the allowing multiples of coexisting substances were investigated. The results show that most common ions do not interfere with the determination of Pb (II). However, there are bigger interferences of Ag^+, Cd^{2+} and Bi^{3+}. In the

determination of real environmental water samples, the disturbances of them could be removed by adding complexion II and dimercaptopropanol according toliterature.

3.5. Analytical application

According to the abovementioned experimental methods, concentration of Pb (II) in three water samples were determined after necessary pretreatment steps. The results show that the recoveries of the method are between 80% and 107%; the relative standard deviation is between 1.8% and 4.6%. This method can fast and accurate determination of trace levels of Pb (II) in the water samples.

Table.3-1. Determination of Lead (II) in Real Samples (n=3)

Sample	Found ($\mu g \cdot mL^{-1}$)	Added ($\mu g \cdot mL^{-1}$)	Total Found ($\mu g \cdot mL^{-1}$)	Recovery (%,n=3)	RSD (%,n = 3)
No.1	ND	0.40	0.35	87.50	1.8
	ND	0.60	0.64	106.68	2.9
	ND	0.80	0.69	86.25	3.1
No.2	ND	0.40	0.32	80.00	4.6
	ND	0.60	0.55	91.66	3.4
	ND	0.80	0.65	81.25	3.1
No.3	0.21	0.40	0.58	92.50	2.2
	0.33	0.60	0.89	93.33	1.8
	0.25	0.80	0.95	87.50	4.3

ND: Not detected

4. Conclusion

In acidic medium, neutral ion-association complex $[PbI_4]^{2-}$ reacted with malachite green resulted in the obvious enhancement of RLS. The concentration of Pb (II) is proportion to the increment of intensity of RLS in a certain range. Based on this, a new method for the determination of Pb (II) was established. The developed method has the advantages of simplicity, rapidity, good selectivity and high sensitivity.

5. Acknowledgements

6. References

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