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DETERMINATION OF LEAD AT NANOGRAM LEVEL IN WATER SAMPLES BY RESONANCE LIGHT SCATTERING TECHNIQUE USING TETRABUTYL AMMONIUM BROMIDE AS A MOLECULAR PROBE

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ABSTRACT. A novel method of chemistry applicable to the determination of trace lead in water samples based on the resonance light scattering (RLS) technique has been developed. In dilute phosphoric acid medium, in the presence of a large excess of I^-, Pb(II) can form $[PbI_4]^{2-}$, which further reacts with tetrabutyl ammonium bromide (TBAB) to form an ion-association compound. This results in significant enhancement of RLS intensity and the appearance of the corresponding RLS spectral characteristics. The maximum scattering peak of the system exists at 402 nm. Under optimum conditions, there is a linear relationship between the relative intensity of RLS and concentration of Pb(II) in the range of 0.04–1.8 μg/mL for the system with a low detection limit of 0.74 ng/mL for Pb(II). Based on this fact, a simple, rapid, and sensitive method has been developed for the determination of Pb(II) at nanogram level by RLS technique using a common spectrofluorimeter. This analytical system was successfully applied to determining trace amounts of Pb(II) in water samples that agree well with the results by atomic absorbance spectrometry (AAS).

KEY WORDS: Lead, Tetrabutyl ammonium bromide (TBAB), Potassium iodide (KI), Resonance light scattering (RLS)

INTRODUCTION

As is well known, heavy metal pollution has been a focus of attention all over the world. Metal ions frequently contained in industrial and municipal wastewater can be harmful to aquatic life and animal health. Due to accumulative toxicity to the human body, lead is one of the most toxic metals to man. There are high levels of Pb(II) in wastewater from manufacturing of storage battery, drainage from lead ore mines, paints, munitions, and petroleum refining. Many methods have been used to determine the content of this toxic heavy metal. However, they have some disadvantages relative sensitivity, selectivity, stability and operation. Consequently, it is an urgent need to develop a simple and sensitive conventional method for measuring lead ion in water samples.

Since Pasternack [1, 2] studied the aggregations of porphyrines using resonance light scattering (RLS) technology, RLS has strongly attracted the interest of analysts and biochemists [3-7] as a promising spectral technique. RLS is a special elastic scattering produced when the wavelength of Rayleigh scattering (RS) is located at or close to the molecular absorption band. According to the macroscopic fluctuation theory, scattering light originates from the fluctuations of the solution refractive index which consists of real and imaginary parts. The Rayleigh scattering law of $I \propto 1/\lambda^4$ [8, 9] is obeyed for the light scattering of the molecular particles 20-fold smaller than the wavelength of the incident beam [8]. However, Rayleigh scattering will deviate from the law and the intensity of some wavelengths will rapidly increase if the wavelength of the incident beam is close to that of the absorption band of the aggregated molecular particles. Recently, RLS has become a useful technique for the determination of

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*Corresponding author. E-mail: fenglingcui@hotmail.com traces of inorganic ions [10, 11], nucleic acids [12, 13], surfactants [14, 15], drugs [16-18] and proteins [19, 20], as well as for the studies of interactions of biopolymers with their probes [21].

Quaternary ammonium salts have been demonstrated to be very effective activators which can strongly affect the activity of enzymes [22] and have also other applications. For example, TBAB has been demonstrated as a very effective reagent for selective extraction of anionic dyes [23] and hexavalent chromium (Cr) [24] from aqueous solution. Also it can be used as a phase transfer catalyst in a biphasic system [25] and a mobile phase in a high-performance liquid chromatographic method [26]. However, up to now, its use for the determination of heavy metals has not yet been paid much attention to. In this paper, we firstly studied the characteristics of RLS spectra of Pb(II)-KI-TBAB system. Suitable reaction conditions of the system and the affecting factors were investigated, as well as the influence of some coexisting substances. Compared with other methods for the quantification of Pb(II), the proposed method does not involve complicated procedures. This method provides a direct way for determining trace amounts of Pb(II) when high levels of potentially interfering compounds are present without any pretreatment procedure. Therefore, the method is useful for determination of Pb(II) in real samples.

EXPERIMENTAL

Materials and apparatus

Stock solution (1.0 mg/mL) of lead ion was prepared by dissolving $Pb(NO_3)_2$ (Tianjin, China) in doubly distilled water and working standard solution (10 μg/mL) was prepared fresh daily by appropriately diluting the stock solution. A 0.15 M stock solution of TBAB (Nanchang, China) and 10% (m/v) KI (Tianjin, China) were prepared by dissolving accurately weighed quantities. To adjust the acidity of the solution, 0.5 M H_3PO_4 (Luoyang, China), 1 M HCl (Zhengzhou, China), 1 M H_2SO_4 (Xinyang, China) and 1 M $HClO_4$ (Beijing, China) solutions were prepared. Surfactants solutions containing 2 g/L of each of the following were prepared: Tween-20 (Solon, Oh, USA), cetyltrimethylammonium bromide (CTMAB) (Shanghai, China), cetylpyridinium bromide (CPB) (Beijing, China), *p*-octyl polyethylene glycol phenyl ether (OP), sodium dodecyl sulfate (SDS) (Shanghai, China) and sodium lauryl sulfonate (SLS) (Tianjin, China).

Water samples were immediately filtered through cellulose nitrate (0.45 μm pore size, 47 mm diameter) and acidified to pH 2 with nitric acid and stored in precleaned polyethylene bottles. All the reagents were of analytical reagent grade and doubly distilled water was used throughout.

RLS spectra were measured on an FP-6200 spectrofluorometer (JASCO, Tokyo, Japan) by scanning simultaneously the excitation and emission monochromators from 300 to 600 nm. Both the excitation and emission slits were set at 5.0 nm. Atomic absorption spectrometric measurements were carried out by a Z-5000 Atomic absorption spectrometer (Hitachi Ltd, Tokyo, Japan).

General procedure

Into a 10 mL volumetric flask, 1.2 mL of 0.5 M H_3PO_4, appropriate amount of 10 μg/mL Pb(II), 1.6 mL of 10% KI, 1.0 mL of 0.15 M TBAB and 1.0 mL of 2 g/L Tween-20 were added successively and diluted to the mark with doubly distilled water. After mixing thoroughly and standing for 10 min, the RLS spectra of the ion-association system were recorded with synchronous scanning at $\lambda_{ex} = \lambda_{em}$ (i.e. $\Delta\lambda = 0$) and measured the RLS intensity I_{RLS} for the ion-association compound and I^0_{RLS} for the reagent blank at its own maximum RLS wavelength; $\Delta I_{RLS} = I_{RLS} - I^0_{RLS.}$

RESULTS AND DISCUSSION

Resonance light scattering spectra

The RLS spectra of the system were recorded by synchronous scanning from 300 to 600 nm. The results are shown in Figure 1. We can see that: (1) under experimental conditions, the RLS intensity of the blank was very small and nearly constant; (2) when Pb(II) was added, the RLS is greatly increased and new RLS spectra appeared; (3) the maximum peak was located at 402 nm. The major reason may be that when TBAB was added, it reacted with $[PbI_4]^{2-}$ to form an ion-association complex and greatly increased the volume of the molecule. The chemical reaction equations are as follows,

$$Pb(II) + 4I^- \rightarrow [PbI_4]^{2-}$$

$$[PbI_4]^{2-} + 2TBAB^+ \rightarrow [PbI_4][TBAB]_2$$

According to the following formula of RLS [27, 28],

$$I_{RLS} = \frac{32\pi^3 V^2 n^2 N}{3\lambda_0^{\ 4}} \left[(\delta_n)^2 + (\delta_k)^2\right]$$

where n is the refractive index of the medium, N is the molarity of the solution, λ_0 is the wavelength of the incident and scattered light, V^2 is the square of molecular volume, δ_n and δ_k are the fluctuations in the real and imaginary components of the refractive index of the particle, respectively. When other factors are constant, I_{RLS} is related to the size of the formed particle and directly proportional to the square of molecular volume (i.e. V^2). With the increase of molecular volume, I_{RLS} was enhanced obviously.

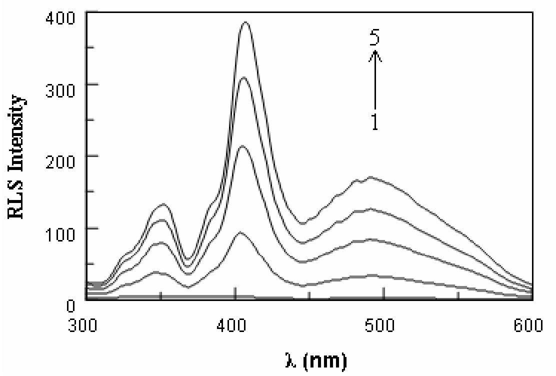

Figure 1. Resonance light scattering spectra of the TBAB-KI-Pb(II) system. Pb(II) from 1 to 5: 0, 0.20, 0.40, 0.60, 0.80 µg/mL. Conditions: H_3PO_4: 0.06 M; KI: 1.6%; Tween-20: 0.20 g/L; TBAB: 0.015 M.

Optimum reaction conditions

Effect of addition sequence and pH. Four acids, H_3PO_4, H_2SO_4, HCl and $HClO_4$ were used to control pH of the solution. The results showed that ΔI_{RLS} of the system in H_3PO_4 solution was the highest, probably because H_3PO_4 acts both as a substrate and a reactant. Therefore, H_3PO_4 solution was selected to control the pH at an optimum concentration of 0.06 M.

Different addition orders of reagents have obviously different effects on the interaction of Pb(II) ion with TBAB. Five types of mixing sequences were investigated. It was found that if the order of reagents addition was H_3PO_4 + Pb(II) + KI + TBAB + Tween-20, both the stability and intensities of RLS signals were better, improving the aggregation of TBAB and the interaction of Pb(II) ion with TBAB. Therefore, this sequence was adopted in subsequent experiments.

Effect of surfactant concentration on the RLS intensity. In order to increase the intensity of RLS, we investigated the effects of cationic surfactants (CTMAB and CPB), anionic surfactants (SLS and SDS) and non-ionic surfactants (Tween-20 and OP) on the RLS intensity of the system. The addition of cationic surfactants resulted in the appearance of precipitation because cationic surfactants react with KI. The RLS intensity of the systems increased with the addition of these surfactants and higher sensitivity achieved when Tween-20 was added. This probably indicates a more steady formation of $[PbI_4][TBAB]_2$ in the presence of Tween-20. So, the surfactant Tween-20 was employed at an optimum concentration of 0.20 g/L for the system (Figure 2).

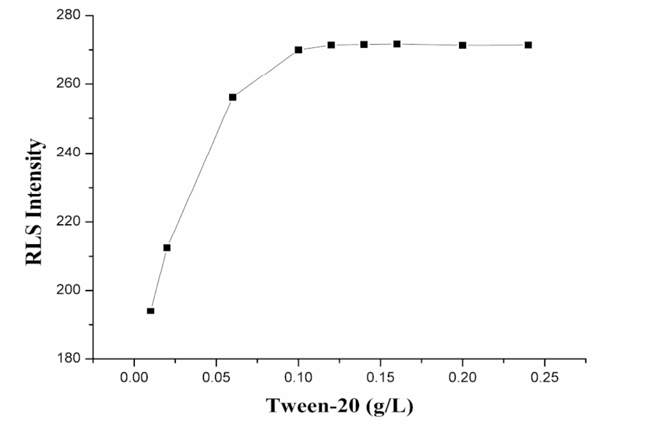

Figure 2. Effect of Tween-20 concentration on the RLS intensity. Conditions: Pb(II): 0.5 µg/mL; H_3PO_4: 0.06 M; KI: 1.6%; TBAB: 0.015 M.

Effect of TBAB concentration. Figure 3 shows the effect of TBAB concentration in the range 0 to 0.03 M on this assay. When the concentration of TBAB was low, the relative intensity of RLS is low due to the incomplete reaction with $[PbI_4]^{2-}$. ΔI_{RLS} reaches maximum when the TBAB concentration was 0.015 M. A further increase in TBAB concentration results in a gradual decrease in ΔI_{RLS}. This may be attributed to molecular absorption by TBAB itself for light scattering. Hence, 0.015 M TBAB was selected for the system.

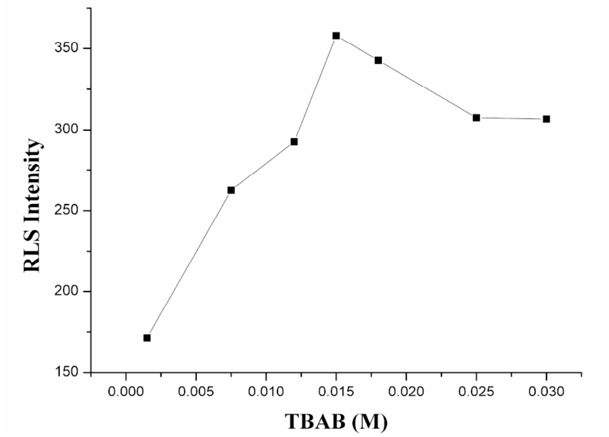

Figure 3. The effect of TBAB concentration on RLS intensity. Conditions: Pb(II): 0.5 µg/mL; H_3PO_4: 0.06 M; KI: 1.6%; Tween-20: 0.20 g/L.

Effect of KI concentration. Figure 4 shows the influence of KI concentration on ΔI_{RLS}. The results showed that the ΔI_{RLS} of the system gradually increased with increasing concentration of KI at first, and ΔI_{RLS} reached a maximum when KI concentration was 1.6%. If KI concentration increased further, ΔI_{RLS} remained relatively stable, indicating complete formation of $[PbI_4][TBAB]_2$. Hence, 1.6% KI was chosen for the system.

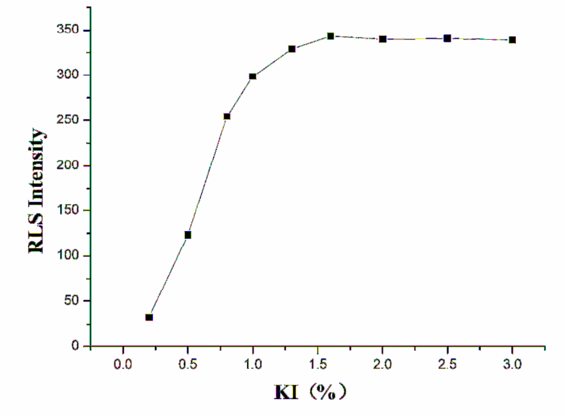

Figure 4. The effect of KI concentration on RLS intensity. Conditions: Pb(II): 0.5 µg/mL; H_3PO_4: 0.06 M; Tween-20: 0.20 g/L; TBAB: 0.015 M.

Effect of temperature and stability of I_{RLS}. Completion of the reaction was studied at room temperature by measuring the RLS intensity of 1.0 µg/mL solution of Pb(II) at 402 nm for a period of 2.0 h after mixing. The results showed that the reaction reached completion within 7 min and RLS intensity remained constant for at least 1.5 h thereafter. When the temperature change was within 5 °C, ΔI_{RLS} remains constant. Thus, this assay did not require crucial temperature and the stability of this assay was reasonable and acceptable for analytical applications. When the temperature increased further, ΔI_{RLS} decreased. The reason might be that the ion-association complex was formed by electrostatic attraction and hydrophobic interaction force. With an increase in temperature, the molecular thermal motion accelerates and surmounts electrostatic attraction and hydrophobic interaction force leading to dissociation of the ion-association complex and a consequent decrease in ΔI_{RLS} of the system.

Effect of ionic strength. The effect of ionic strength on the RLS intensities of the system was investigated. This was studied by increasing the concentration of NaCl while keeping the TBAB, KI, Pb(II) concentrations and the pH constant. It was observed that I_{RLS} decreased with an increase in ionic strength. It revealed that an increase in salt concentration causes a decrease in the combination of TBAB with $[PbI_4]^2$. This effect may be explained as a competition between Cl^- and $[PbI_4]^{2-}$ for the same binding sites on TBAB. Therefore, in subsequent experiments, no NaCl solution was added to simplify the experiment.

Effect of organic solvent. Solvents are widely applied in the field of analytical chemistry. Here, we investigated the effect of ethanol as a solvent on the RLS intensity by increasing its concentration. The results showed a decrease in the RLS intensity of this system with the addition of ethanol. The reason may be that the presence of ethanol increases the solubility of the ion-association complex.

Effects of coexisting ions. The influence of coexisting substances on the determination of 0.5 μg/mL Pb(II) was investigated and the results are summarized in Table 1. It can be seen from Table 1 that most of potentially interfering substances have little effect on the determination of Pb(II) within the permissible ± 5% error. Though the relative error is out of the permissible range, Fe^{3+} can be allowed only at low relative concentration and the interference of it can be eliminated by addition of enough ascorbic acid.

Table 1. Effects of potentially coexisting ions on the determination of Pb^{2+} (0.5 μg/mL).

Coexisting ion	Tolerance limit (μg/mL)	Relative error (%)	Coexisting ion	Tolerance limit (μg/mL)	Relative error (%)
F^-	250	-4.96	Ni^{2+}	100	-4.43
NO_3^-	350	-3.33	Co^{2+}	1000	-4.83
SO_3^{2-}	400	-3.49	Al^{3+}	20	-4.22
CO_3^{2-}	100	-4.91	Cu^{2+}	17	-4.12
$Fe^{3+\,a}$	30	-6.12	Hg^{2+}	10	4.78
SO_4^{2-}	500	-3.06	Mn^{2+}	450	-4.25
NH_4^+	35	-3.20	Ba^{2+}	1500	-4.82
HSO_4^-	400	-4.30	Ca^{2+}	20	-4.36
$C_2O_4^{2-}$	250	-5.01	Mg^{2+}	50	-3.86
HCO_3^-	600	-3.22	Cd^{2+}	2	4.35

[a] After adding ascorbic acid.

Calibration curve and determination of Pb(II) in samples

Under the optimum conditions, the ΔI_{RLS} values of the complex were measured at the maximum scattering wavelength, and the calibration curve of ΔI_{RLS} against concentration of Pb(II) was constructed. The enhanced RLS intensity was directly proportional to the concentration of Pb(II) in the range of 0.04–1.8 μg/mL and the regression equation was calculated as $\Delta I_{RLS} = 5.87 + 488C$ (μg/mL) with regression coefficient $r = 0.997$. The detection limit was 0.74 ng/mL, which was calculated as $3S_0/S$, where S_0 is the standard deviation (SD) of the blank measurements ($n =$

11) and *S* the slope of the calibration curve. The RSD for 11 determinations of 1.0 µg/mL Pb(II) was 2.0%. The precision of the determination was studied and the relative standard deviation was calculated on the basis of five repeating measurements. In addition, the accuracy of the developed method was checked by comparison of the results obtained by RLS method to those found using AAS as a reference method (Table 2). The results indicate absence of significant difference between the two methods.

Table 2. Analytical results of real samples.

Samples	AAS method	RLS method		
	Found (µg/mL, n = 5) ± SD	Found (µg/mL, n = 5) ± SD	Added (µg/mL)	Recovery (%, n = 5) ± SD
River water	0.58 ± 0.024	0.55 ± 0.01	0.50	103 ± 0.01
Wastewater	0.76 ± 0.008	0.80 ± 0.012	1.00	97.2 ± 0.031
Drinking water	0.15 ± 0.041	0.13 ± 0.003	0.20	104 ± 0.012
Mineral Water	0.41 ± 0.01	0.44 ± 0.01	0.50	95.6 ± 0.04

From the results above, it can be concluded that this method has a low detection limit and high sensitivity. Compared with the reported analytical methods for Pb(II) [29-35] (Table 3), the RLS method is highly sensitive and selective, and can be regarded as one of the best analytical methods for the determination of Pb(II) up to now.

Table 3. Comparison with other methods for the determination of Pb^{2+} in water samples.

Method	Sample	Linear range (µg/mL)	Detection limit (ng/mL)	Reference
1	Malaysian natural waters	–	8270	29
2	Sea water samples	–	0.83	30
3	Drinking water samples	0.01–0.1	2.00	31
4	Drinking water samples	0.01–0.1	10.0	31
5	Drinking water, sea water sample	–	10.0	32
6	Tap water, river water, sea water	0.001–0.16	1.10	33
7	Water samples	0.02–3.11	2.07	34
8	Seawater, mineral Water	–	16.0	35

1. Flow injection system coupled to ion chromatography. 2. Electrothermal atomic absorption spectrometry. 3. Flow injection systems with anodic stripping voltammetric detection. 4. Sequential injection systems with anodic stripping voltammetric detection. 5. Flame atomic absorption spectrometry. 6. Flame atomic absorption spectrometry. 7. Differential pulse stripping voltammetry. 8. Flame atomic absorption spectrometry.

CONCLUSIONS

Based on the fact that the weak resonance light scattering intensity of Pb(II) is greatly enhanced in the presence of TBAB, we developed a new method using TBAB as a molecular probe for the determination of trace Pb(II) at nanogram level. Compared with other common methods, the RLS technique is rapid, convenient, sensitive, and can be accomplished with a common fluorescence spectrometer by using inexpensive and safe reagents. This method can be successfully applied to the determination of Pb(II) in wastewater samples. The results obtained are satisfactory, and are in agreement with those of AAS.

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