RESONANCE RAYLEIGH SCATTERING SPECTRA OF THE LEAD–XYLENOL ORANGE–CRYSTAL VIOLET SYSTEM AND THEIR ANALYTICAL APPLICATIONS[**]

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    A new method for determining lead by resonance Rayleigh scattering (RRS) has been proposed and its operation mechanism has been discussed. In pH 5.0 HAc-NaAc buffer solution, Pb(II) reacted with xylenol orange (XO) to form a chelating anion ($[Pb (H_2In)]^{2-}$), which further reacted with crystal violet (CV) to form ternary ionic complexes, resulting in the enhancement of RRS intensity. The RRS intensity increases linearly with the concentration of Pb(II) in the range of 2.00×10^{-3}–2.00×10^{-2} mg/L under optimal experimental conditions along with the detection limit of 9.2×10^{-5} mg/L. This method is a promising approach for the selective and sensitive determination of Pb(II) in tea.

    Keywords: *resonance Rayleigh scattering, lead, xylenol orange, crystal violet.*

СПЕКТРЫ РЕЗОНАНСНОГО РЭЛЕЕВСКОГО РАССЕЯНИЯ СИСТЕМЫ СВИНЕЦ—КСИЛЕНОЛОВЫЙ ОРАНЖЕВЫЙ—КРИСТАЛЛИЧЕСКИЙ ФИОЛЕТОВЫЙ И ИХ АНАЛИТИЧЕСКИЕ ПРИМЕНЕНИЯ

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    Предложен метод определения свинца по резонансному рэлеевскому рассеянию (РРР) и обсужден механизм его действия. В буферном растворе HAc-NaAc с pH 5.0 проведена реакция Pb(II) с ксиленоловым оранжевым с образованием хелатного аниона ($[Pb (H_2In)]^{2-}$), который реагирует с кристаллическим фиолетовым с образованием тройных ионных комплексов, что приводит к усилению интенсивности РРР. Интенсивность РРР линейно возрастает с концентрацией Pb(II) в диапазоне 2×10^{-3}—2×10^{-2} мг/л при оптимальных условиях эксперимента, обеспечивая предел обнаружения 9.2×10^{-5} мг/л. Метод применен для селективного и чувствительного определения Pb(II) в чае.

    Ключевые слова: *резонансное рэлеевское рассеяние, свинец, ксиленоловый оранжевый, кристаллический фиолетовый.*

Introduction. Lead is widely used in many fields because of its malleability and ductility, but it is also a toxic heavy metal and it causes great harm to the human body. Therefore, it is very important to accurately determine the lead content. Many reported methods are based on the detection of lead(II), including spectrophotometry [1–4], atomic spectrometry [5, 6], fluorescence spectrophotometry [7], and graphite furnace atomic absorption spectrometry [8–10]. Resonance Rayleigh scattering (RRS) is a new spectral analysis technique developed in the 1990 s [11, 12], which has attracted much attention because of its simplicity, short response time, and high sensitivity. In recent years, it has been increasingly applied to the study and determination of metal ions [13–16]. Xylenol orange (XO) and crystal violet (CV) are triphenylmethane color reagents. A new method was developed for the determination of lead by resonance Rayleigh scattering in the presence of polyvinyl alcohol (PVA). The method is simple, convenient and can be applied to the determination of trace lead in tea.

Experimental. In our experiment, we used an F-7000 fluorescent spectrophotometer (Hitachi Company, Japan), a CRT-970 fluorescence spectrophotometer (Shanghai Sanke instrument Company, China) and a U-3900H UV-Vis spectrophotometer (Hitachi Company, Japan). The pH was measured by a pHS-3C meter (Shanghai Leici Instruments Company, China).

The stock solution of Pb(II) (100 mg/L) was prepared as follows. We used 0.1599 g of $Pb(NO_3)_2$ (Beijing Jiangxing Chemical Factory, China) dissolved in 9.00 mL of distilled water and 1.00 mL of a concentrated nitric acid solution diluted to 1000 mL. The concentration of Xylenol Orange (XO) (Shanghai General Chemical Reagent Factory, China) was 2.53×10^{-4} mol/L, whereas the concentration of Crystal Violet (CV) (Tianjin Fuchen Chemical Reagent Factory, China) was 2.45×10^{-5} mol/L. The other solutions were polyvinyl alcohol (0.4% aqueous solution) (Tianjin Fuchen Chemical Reagent Factory, China) and HAc-NaAc buffer solution (adjusted pH 5.0 with a pH meter). All reagents were of analytical pure, and the water used was double-distilled water.

Procedures. A 1.00 ml portion of HAc-NaAc buffer solution, 0.60 mL of Xylenol Orange, 1.40 mL of Crystal Violet, and a suitable amount of Pb(II) were added to a 10 ml calibrated flask. The mixture was diluted to the mark with water and mixed thoroughly. The RRS spectra were recorded with synchronous scanning at $\lambda_{em} = \lambda_{ex}$. After 30 min, The RRS intensity I_{RRS} for the reaction product and I_0 for the reagent blank were measured at the maximum scattered wavelength (Fig. 1). Herein, $\Delta I_{RRS} = I_{RRS} - I_0$. Figure 1 shows the resonant Rayleigh scattering spectra of the system. The RRS intensity of the XO-Pb(II), CV-Pb(II), and CV-XO systems is very weak. When the CV solution, XO solution, and Pb(II) coexist, the RRS intensity undergoes a significant change, and the strongest peak is at 647 nm. Therefore, we selected 647 nm as the measurement wavelength. The RRS intensity of the system increases with increase in Pb(II) concentration, which indicates that the system can be used for the detection of Pb(II) with high sensitivity.
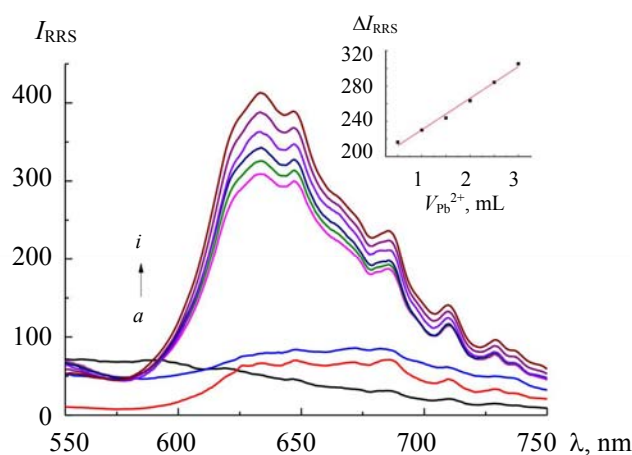

Fig. 1. Resonance Rayleigh scattering spectra of the system: a) XO+Pb(II); b) CV+Pb(II); c) CV+XO;
d) c+2.00×10^{-3} mg/L Pb(II); e) c+3.50×10^{-3} mg/L Pb(II); f) c+5.00×10^{-3} mg/L Pb(II);
g) c+1.00×10^{-2} mg/L Pb(II); h) c+1.50×10^{-2} mg/L Pb(II); i) c+2.00×10^{-2} mg/L Pb(II).

Results and discussion. *Effect of pH.* If the pH value is too high, the amphoteric substance $Pb(OH)_2$ is easily formed, which is unfavorable to the formation of ternary complex. XO is an excellent indicator in acidic solutions. CV exists in the form of a monovalent cation (CV^+) in weakly acidic and neutral solution, which facilitates the formation of a complex, whereas it exists as a lactone structure in an alkaline solution. Therefore, a weak acid buffer solution of HAc-NaAc should be added to the system. As shown in Fig. 2, pH 5.0 HAc-NaAc is the most suitable buffer solution, so it was used in the experiment.
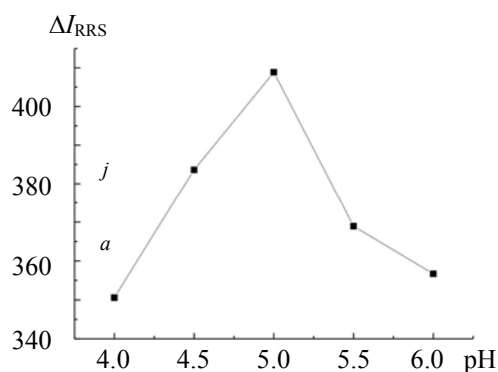

Fig. 2. The effect of pH on the RRS intensity of the system.

Effect of CV and XO. The effect of the dosage of CV and XO on the reaction system was studied. As shown in Fig. 3, the RRS intensity was the largest and the most stable when the amount of XO was between 0.30 and 2.00 mL, so 0.60 mL of XO was chosen in the final experiment. In this experiment, the amount of CV was suitable for 0.30–2.50 mL, and CV and OX would be combined with each other in a corresponding proportion. A larger steric hindrance required an excess of XO to make the system react completely, but CV excessively dimerized, and the resulting self-RRS affected the RRS intensity of the system. Therefore, the addition volume of CV was 1.40 mL.
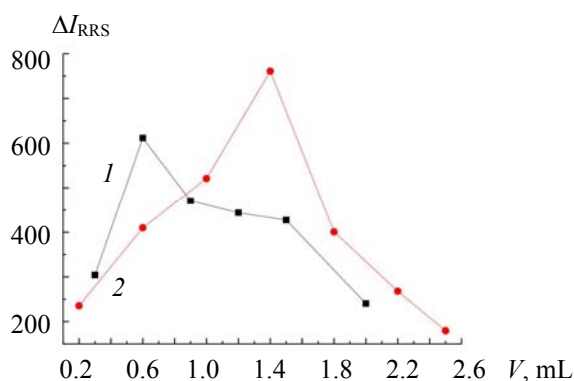

Fig. 3. The effect of XO (1) and CV (2) dosage on the RRS intensity of the system.

Effect of surfactants. The PVA has a solubilizing effect, which makes the solution more stable. If it is too little, the effect of solubilization cannot be achieved. However, if it is excessive, the foam produced by PVA will affect the measurement of the RRS intensity of the system. In this experiment, the amount of PVA was 0.50 mL.

Work curve and detection limit. Under the optimal conditions, the RRS spectra of the system were measured at their maximum scattering wavelength of 647 nm. The results showed that the RRS intensity of the solution increased with increasing concentrations of Pb(II), and there was a good linear relationship between the ΔI_{RRS} and the concentrations of Pb(II) in the range of 2.00×10^{-3} to 2.00×10^{-2} mg/L. The detection

limit is 9.20×10^{-5} mg/L. The linear regression equation has the form $\Delta I_{RRS} = 279.14 + 74.29 \rho_{Pb(II)}$(mg/L) ($R^2 = 0.9932$).

Selectivity of the method. According to the procedure, the influence of foreign substances on the determination of lead ion was investigated within a relative error of $\pm 5\%$. The RRS intensity of different ions (Ba^{2+}, Mg^{2+}, K^+(5000); Ca^{2+}, Mn^{2+}, Ni^{2+}(3000); Na^+, Cl^-, F^-(2000)) was studied. After Hg^{2+} and Zn^{2+} were adsorbed and eluted with sulfhydryl cotton with different acidity, the influence on the determination result could be eliminated. The interference of Cu^{2+} and Fe^{3+} was more serious; 0.1% of ascorbic acid could prevent Fe^{3+} from interfering up to 1000 times, while 0.2% of thiourea could increase the interference multiple of Cu^{2+}.

Discussion of the quenching mechanism. At pH 5.0-6.0, XO mainly exists in the form of H_2In^{4-}. In the pH 5.0 HAc-NaAc buffer solution, the red complex ($[Pb(H_2In)]^{2-}$) formed by XO and Pb(II) reacted with CV^+ (CV exists as CV^+ in neutral or weak acid solution) to form ternary ion complexes through electrostatic interaction and hydrophobic force. The hydrophobic interface between the complexes and the solution increased the RRS intensity of the system. As is shown in Fig. 4, it is caused by the reactions in the system.
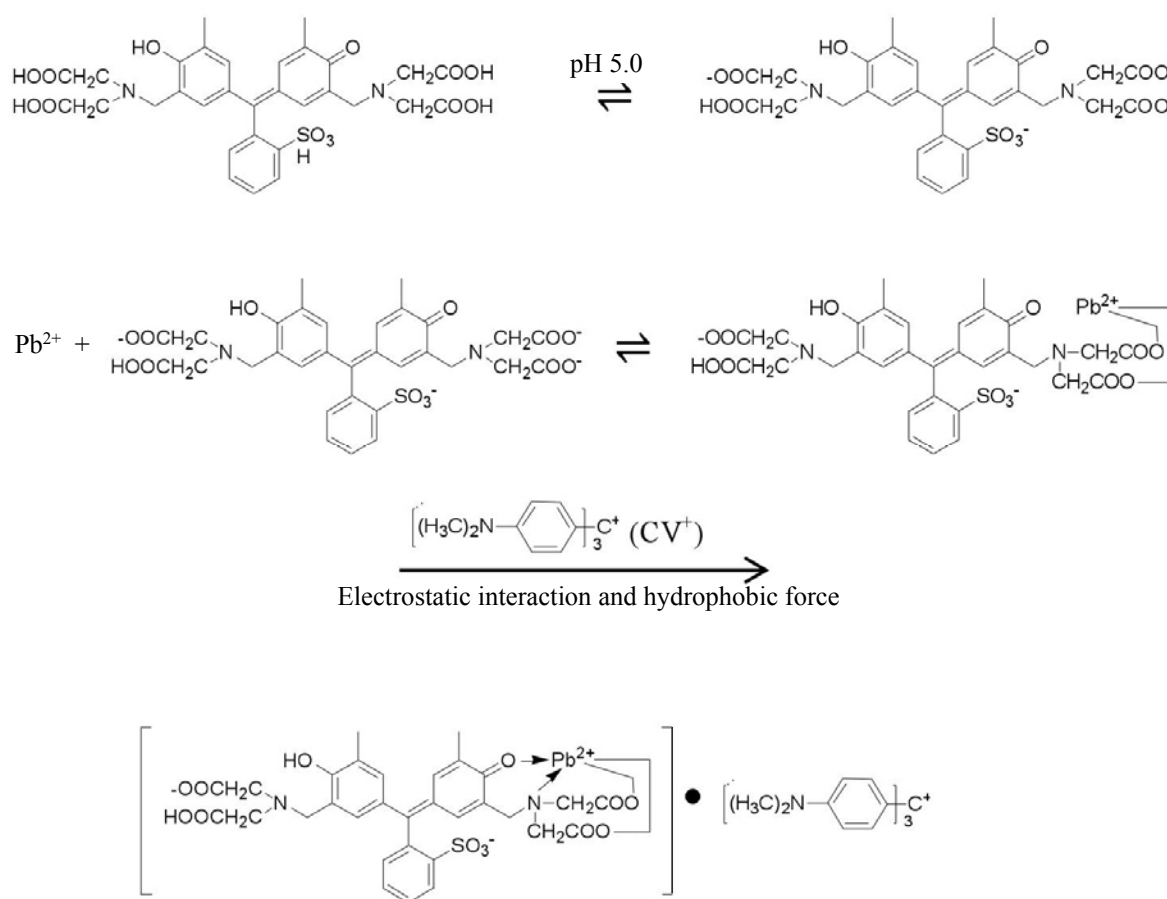

Fig. 4. Mechanism of the reaction.

Detection of Pb(II) in tea. We used the obtained results to determine Pb(II) in tea. For comparison, we applied a standard addition method to measure the concentration of Pb(II) in tea. The results are summarized in Table 1. Before the measurement, according to [17], the 0.5000 g sample was crushed, dissolved, and filtered. Hg^{2+}, Zn^{2+}, and other interfering ions were adsorbed and eluted with sulfhydryl cotton, then heated and concentrated to a volumetric flask of 500 mL.

TABLE 1. Results of the Determination of Pb(II) in Tea Samples

Sample	Found, mg/kg	Added,mg/kg	Total found,mg/kg	Recovery,%	RSD,%
Tea 1	3.17	1.50	4.62	96.7	2.08
Tea 2	2.04	1.50	3.45	94.3	1.26

Conclusion. We have developed a novel method for the determination of trace amounts of Pb(II) based on the formation of a lead-xylenol orange-crystal violet system by RRS. The linear relationship between the RRS intensity and the Pb(II) concentration was established under optimal experimental conditions. This phenomenon further enlarges the study and application range of the RRS method and provides new information for a study based on RRS.

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