Available online at www.sciencedirect.com
SCIENCE DIRECT®

Talanta 65 (2005) 501–504

Talanta

www.elsevier.com/locate/talanta

Determination of trace mercury by solid substrate room temperature phosphorescence quenching method based on lead carboxymethyl cellulose ($Pb(CMC)_2$) particles containing luminescent salicyl fluorones molecules

Jia-Ming Liu[a,*], Ai-Hong Wu[a], Huan-Huan Xu[a], Qing-Hua Wang[a], Long-Di Li[b], Guo-Hui Zhu[c]

[a] *Department of Chemistry, ZhangZhou Normal College, ZhangZhou 363000, China*
[b] *Department of Chemistry, Tsinghua University, Beijing 100084, China*
[c] *Department of Food and Chemical Engineering, ZhangZhou Institute of Technology, ZhangZhou 363000, China*

Received 31 January 2004; accepted 29 June 2004
Available online 20 August 2004

Abstract

Luminescent particles of lead carboxymethyl cellulose ($Pb(CMC)_2$), which contains salicyl fluorones (THBF), $Pb(CMC)_2$-THBF, were synthesized by sol–gel method. $Pb(CMC)_2$-THBF can emit intense and stable solid substrate room temperature phosphorescence (SS-RTP) on filter paper. EDTA can chelate the Pb^{2+} in $Pb(CMC)_2$-THBF, causing it decompose into aqueous soluble components PbY^{2-}, CMC^- and THBF, and these components can react with Hg^{2+} to form $(CMC)_2Hg$-THBF, causing decrease of phosphorescence intensity. Based on the facts above, a new method for the determination of trace mercury by SS-RTP quenching method was established. The linear range of this method is 2.0–40.0 fg spot^{-1} (5.0–100.0 pg ml^{-1}) of Hg^{2+}, with a detection limit (LD) of 0.26 fg spot^{-1}, and the regression equation of working curve is $\Delta I_p = 13.02 + 1.165 m_{Hg^{2+}}$ (fg spot^{-1}, 0.4 µl spot^{-1}), $r = 0.9994$. This method has been applied to the determination of trace mercury in water sample with satisfactory results. The mechanism of SS-RTP emission is also discussed.

Keywords: Salicyl fluorones; Carboxymethyl cellulose; Solid substrate room temperature phosphorescence; Quenching; Mercury

1. Introduction

The synthesis [1] and application [2] of sodium carboxymethyl cellulose (NaCMC) have been reported before, but the synthesis, SS-RTP property and analysis application of $Pb(CMC)_2$-THBF have not been reported. During recent years many methods for the determination of trace mercury have been reported, such as floatation separation of mercury (LD: 6.8×10^{-9} g ml^{-1}) [3] with ammonium thiocyanate–malachite green–water liquid–solid system, Hg^{2+}-sulfourea-α,α-dipyridyl-$Fe(CN)_6$ enzyme catalytic kinetic photometry (LD: 5.0×10^{-10} g ml^{-1}) [4], Hg^{2+} potassium iodated persulfate amaranth retardation color fading photometric analysis (LD: 2.0×10^{-9} g ml^{-1}) [5], and Hg^{2+}-KI-azureI system flow injection catalytic photometry (LD: 2.5×10^{-7} g ml^{-1}) [6]. Photometric analysis using salicyl fluorones as chromogenic agent such as Cr(VI)-THBF-CTMAB ($\varepsilon = 1.2 \times 10^5$ l mol^{-1} cm^{-1}) [7], Mn^{2+}-THBF-CTMAB ($\varepsilon = 1.31 \times 10^5$ l mol^{-1} cm^{-1}) [8]. Using NaCMC as precursor and Pb^{2+} as precipitant, we synthesized luminescent particles of $Pb(CMC)_2$-THBF by sol–gel method, which can emit intense and stable solid substrate room temperature phosphorescence on filter paper. EDTA can chelate the Pb^{2+} in $Pb(CMC)_2$-THBF, causing it decompose into aqueous soluble components PbY^{2-}, CMC^- and

---

[*] Corresponding author. Tel.: +86 5962591352; fax: +86 5962591352.
E-mail address: zzsyliujiaming@163.com (J.-M. Liu).

0039-9140/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2004.06.036

THBF, and these components can react with Hg^{2+} to form $Hg(CMC)_2$-THBF, causing the quenching of room temperature phosphorescence of $Pb(CMC)_2$-THBF. Based on the facts above, a new method for the determination of trace mercury by SS-RTP quenching method was established, with a detection limit of 0.26 fg $spot^{-1}$ (6.5×10^{-13} g ml^{-1}), which is 1.3×10^3 times lower than the lowest detection limit [4] reported before. This sensitive, rapid and repeatable method has been applied to the determination of trace mercury in water sample successfully.

2. Experimental

2.1. Apparatus and reagent

Perking Elmer LS-55 luminescence spectrophotometer (main parameters are—delay time: 0.1 ms; gate time: 2.0 ms; cycle time: 20 ms; flash count: 1; Ex. slit: 10 nm; Em. slit: 15 nm; scan speed: 1500 nm min^{-1}); pHS-3B precision acidometer (Shanghai Medical Laser Instrument Plant); 85-1 constant temperature magnetic stirrer (ShenZhen Tian-nan-hai-bei Company); AE240 electronic analytical balance (Mettler-Toledo Instruments Shanghai Company); 0.5 μl flat head micrometer syringe (Shanghai Medical Laser Instrument Plant).

1.00 mg ml^{-1} $Hg(NO_3)_2$ primary standard reagent (GSBG 62069-908001); 1.0 μg ml^{-1} Hg^{2+} working solution (diluted from Hg^{2+} primary standard reagent, and it is diluted to 0.1 ng ml^{-1} before used); 0.1% (w/v) NaCMC solution; 1.0×10^{-4} mol l^{-1} THBF solution; 5.0×10^{-3} mol l^{-1} Pb^{2+} solution; 1% (w/v) EDTA solution; thrice distilled water. All the reagents are AR (analytical reagent) grade, except that Hg^{2+} is primary standard.

Filter paper (HangZhou Xin-Hua Paper Corporation) is precut into small wafers [diameter (Φ) = 15 mm], with a ring indentation (Φ = 4.0 mm) at the center of each wafer made by a standard pinhole plotter; acetylcellulose membrane, nitrocellulose membrane and polyamide membrane (Lu-qiao-si-jia Biochemical Plastic Plant).

2.2. Preparation of $Pb(CMC)_2$-THBF particle

To 50.00 ml of NaCMC solution, 50.00 ml of THBF solution was added, and then 10.00 ml of Pb^{2+} was added dropwise. Standing for 10 min to ensure precipitate completely, the mixture was centrifuged and the solid was washed until there was no lead ion (test by sulfuric acid). After dried and grinded, rose powder of $Pb(CMC)_2$-THBF was obtained.

2.3. Measurement of phosphorescence

100 mg of $Pb(CMC)_2$-THBF dry powder was dissolved in 1% EDTA solution and then diluted to 100.0 ml; to a 10 ml cuvette, 1.00 ml of above solution and some mercury were added, then diluted to scale graduation line and mixed homogeneously, then standing at room temperature for 10 min. Filter papers (Φ = 15 mm) were immersed in $Pb(Ac)_2$ solution (1.0 mol l^{-1}) for 10 s and then dried at 90 ± 1 °C for 2 min. A 0.4 μl drop of test solution was suspended onto the indentation center of filter paper by a 0.5 μl flat head micrometer syringe and then the paper wafer was dried at 90 ± 1 °C for 2 min. The phosphorescence intensity was measured directly at wavelengths $\lambda_{ex}/\lambda_{em}$ = 456/625 nm. The signal of filter paper substrate is defined as the background intensity (I_{p0}), the signal of $Pb(CMC)_2$-THBF-EDTA system (without Hg^{2+}) is defined as reagent blank intensity (I_{p1}), the signal of $Pb(CMC)_2$-THBF-EDTA-Hg^{2+} system is defined as sample intensity for test solution (I_p). Then calculate ΔI_p ($=I_p - I_{p1}$) and the sample/background ratio ($=I_p/I_{p0}$).

3. Results and discussion

3.1. Phosphorescence and fluorescence spectra

The phosphorescence and fluorescence spectra of the sample solution are shown in Figs. 1 and 2, respectively. Results show that $Pb(CMC)_2$-THBF can emit intense and stable solid substrate room temperature phosphorescence (SS-RTP) on filter paper at wavelengths $\lambda_{ex}/\lambda_{em}$ = 468/634 nm. When $Pb(CMC)_2$-THBF was dissolved by EDTA and Hg^{2+} was added to the system, the phosphorescence intensity was decreased (Fig. 1, curve 2,2′ and 3,3′), and the $\lambda_{ex}/\lambda_{em}$ moved to 456/626 nm, which was chosen as the working wavelength for the determination of trace Hg^{2+}. Both $Pb(CMC)_2$-THBF-EDTA and $Pb(CMC)_2$-THBF-EDTA-Hg^{2+} system can emit fluorescence, their $\lambda_{ex}/\lambda_{em}$ are 450/534 and 449/533 nm, respectively (Fig. 2). There are obvious differences between the fluorescence and phosphorescence spectra.

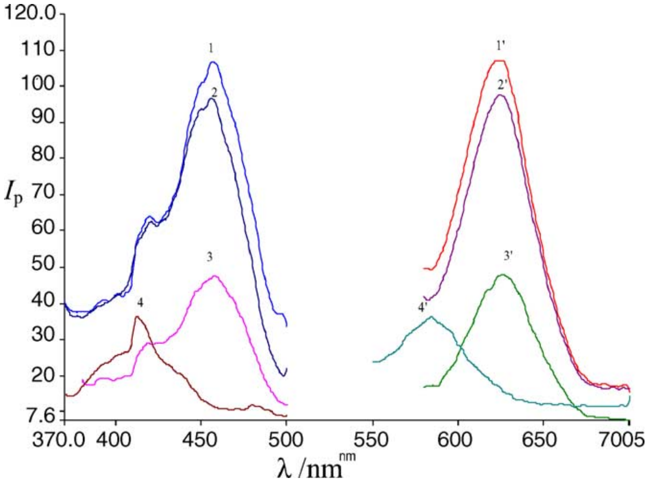

Fig. 1. Room temperature phosphorescence spectra: 1,1′ 1.00 ml $Pb(CMC)_2$-THBF-EDTA; 2,2′ 1,1′ + 0.050 ng Hg^{2+}; 3,3′ 1,1′ + 1.00 ng Hg^{2+}; 4,4′ filter paper.

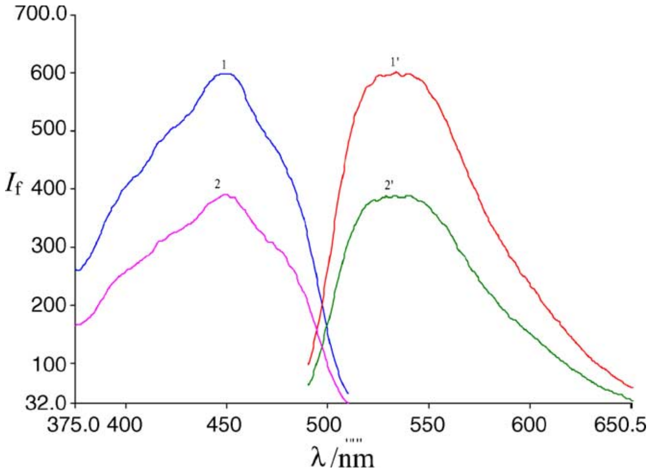

Fig. 2. Fluorescence spectra: 1,1′ 1.00 ml $Pb(CMC)_2$-THBF + 2.00 ml EDTA; 2,2′ 1,1′ + 1.00 ng Hg^{2+}.

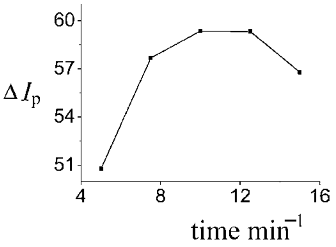

Fig. 3. Effect of time on ΔI_p.

Like Hg^{2+}, other ions such as Cu^{2+}, Ag^+ and Pd^{2+} can also cause quenching of SS-RTP of $Pb(CMC)_2$-THBF in the presence of EDTA, and their $\lambda_{ex}/\lambda_{em}$ are 468/637, 451/621 and 443/614 nm respectively. This indicates that $Pb(CMC)_2$-THBF can also be used to analyze trace Cu, Ag or Pd.

3.2. Optimum measurement condition

3.2.1. Selecting solid substrate

For a system containing 0.10 ng ml^{-1} of Hg^{2+}, the phosphorescence intensity of sample (I_p) and background (I_{p0}) on four different kinds of solid substrates were measured at wavelengths $\lambda_{ex}/\lambda_{em}$ = 468/637 nm. Results showed that the sample/background intensity ratios (I_p/I_{p0}) are 3.0, 2.6, 1.9 and 1.4, for filter paper, nitrocellulose, acetylcellulose and polyamide membrane, respectively. So filter paper was chosen as the solid substrate in the following experiment for its highest I_p/I_{p0} ratio.

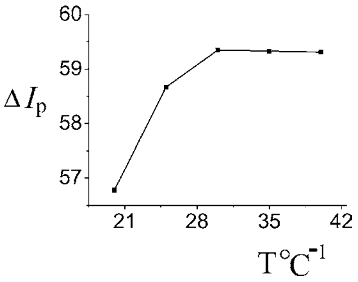

Fig. 4. Effect of temperature on ΔI_p.

3.2.2. Optimization of the concentration of reagents

For a system containing 0.10 ng ml^{-1} of Hg^{2+}, the volumes of different reagents were changed respectively. Results showed that when the volume and concentration were 5.00 ml of 0.1% NaCMC, 5.00 ml of 1.0×10^{-4} mol l^{-1} THBF alcohol solution, 2.00 ml of 5.0×10^{-3} mol l^{-1} Pb^{2+} solution and 2.00 ml of 1.0% EDTA solution, ΔI_p reached the maximum.

3.2.3. Heavy atom effect

For a system of 0.10 ng ml^{-1} Hg^{2+}, the effects of different heavy atoms such as Pb^{2+}, Ag^+, Cu^{2+}, I^- on the signal/noise ratio of the system were examined. The result showed that the signal/noise ratios were 3.0, 2.7, 2.4, 2.8 for Pb^{2+}, Ag^+, Cu^{2+}, I^- as outside heavy atom, respectively. So we can add Pb^{2+} to improve the intensity of SS-RTP.

3.2.4. Time and temperature for reaction and drying

The experiment showed that under the optimal condition above, when the reaction was conducted at 30 °C for 10 min, its ΔI_p reached max and remained constant (Figs. 3 and 4). Before the measurement of phosphorescence, the filter paper was immersed in $Pb(Ac)_2$ solution for 10 s, then dried at 90 ± 1 °C for 2 min, then a ring indentation was made at the center of the filter paper. The sample solution was suspended onto the indentation of the filter paper, and then dried at 90 ± 1 °C for 2 min. Under such conditions the ΔI_p reached maximum.

3.3. Analytical parameters

The content of Cu^{2+}, Hg^{2+}, Ag^+ and Pd^{2+} were determined under the optimal condition described above. The upper and lower detection limits were measured repeatedly for eight times, and the results were listed in Table 1.

Table 1
Working curve, liner range, detection limit (calculated by 3Sb/*k*, *n* = 11) and precision

Ion	Liner range (fg spot^{-1}) (pg ml^{-1})	Regression equation (n = 6) (fg spot^{-1})	Cornecation coefficient (r)	Detection limit (fg spot^{-1}) (pg ml^{-1})	R.S.D. (n = 8) (%)
Cu^{2+}	2.0–40.0 (5.0–100.0)	$\Delta I_p = 21.38 + 0.9640 m_{Cu^{2+}}$	0.9995	0.15 (0.375)	3.6–4.0
Hg^{2+}	2.0–40.0 (5.0–100.0)	$\Delta I_p = 13.03 + 1.165 m_{Hg^{2+}}$	0.9994	0.12 (0.30)	3.2–4.5
Ag^+	8.0–40.0 (20.0–100.0)	$\Delta I_p = 12.56 + 0.5527 m_{Ag^+}$	0.9992	2.2 (5.5)	3.5–4.6
Pd^{2+}	1.6–20.0 (4.0–50.0)	$\Delta I_p = 17.95 + 0.7847 m_{Pd^{2+}}$	0.9989	0.38 (0. 95)	3.4–4.0

Table 2
Attenuation curve and the lifetime of phosphorescence

Ion	Attenuation curve	Cornecation coefficient (r)	Lifetime phosphorescence (ms)
Cu^{2+}	$\ln I_p = 3.2829 - 0.01136t$ (ms)	−0.9937	88.03
Hg^{2+}	$\ln I_p = 3.28 - 0.01028t$ (ms)	−0.9945	97.28
Ag^{+}	$\ln I_p = 3.3311 - 0.01195t$ (ms)	−0.9942	83.68
Pd^{2+}	$\ln I_p = 3.3164 - 0.00911t$ (ms)	−0.9948	109.77

Table 3
Analytical results of Hg^{2+} in samples

Sample	Average found ($\mu g\,l^{-1}$)	RSD (%)	Added ($\mu g\,l^{-1}$)	Recovery (%)	Dithizone ($\mu g\,l^{-1}$)
River water	5.16	2.7	0.50	100.6	5.20
Well water	2.87	2.3	0.30	98.0	2.81
Rain water	5.58	2.8	0.60	101.0	5.64

3.4. *The lifetime of phosphorescence*

For samples containing 40.0 fg spot^{-1} of Cu^{2+}, Hg^{2+}, Ag^{+} or 20.00 fg spot^{-1} of Pd^{2+}, the phosphorescence lifetime (τ) was obtained by phosphorescence attenuation method respectively. The lifetime of phosphorescence was calculated according to the method described in literature [9]. The results are listed in Table 2.

3.5. *Interference experiment*

To determine sample containing 0.10 ng ml^{-1} Hg^{2+}, the allowed concentration of coexistent ions ($E_r = \pm 5\%$) are as following: Na^+, K^+, NH_3, F^-, Cl^-, Br^-, S^{2-}, ${SO_3}^{2-}$, ${SO_4}^{2-}$ (6.0×10^3); Ni^{2+}, Mn^{2+}, ${CO_3}^{2-}$, ${PO_4}^{3-}$, ${C_2O_4}^{2-}$ (5.5×10^2); ${NO_2}^-$, ${NO_3}^-$, SCN^- (3.4×10^2); Cd^{2+}, Bi^{3+}, Pb^{2+} (2.7×10^2); Ca^{2+}, Mg^{2+}, Cr^{3+}, Fe^{3+} (1.8×10^2); Co^{2+}, Al^{3+}, Fe^{2+}, Zn^{2+} (120).

3.6. *Analysis of samples*

10.00 ml of river water, well water and rain water were pipetted and diluted to 250 ml, respectively. A standard addition recovery rate experiment and a comparative test with dithizone were also carried out. The analytical results for Hg^{2+} are listed in Table 3.

3.7. *The mechanism for SS-RTP emission*

Using sodium carboxymethyl cellulose (NaCMC) and THBF as precursor, and Pb^{2+} as precipitant $Pb(CMC)_2$-THBF particles were synthesized by sol–gel method. The particle can emit strong and stable solid substrate room temperature phosphorescence on filter paper under the perturbation effect of Pb^{2+} ion. The possible reaction [2] is

$$2\mathrm{NaCMC} + \underset{\text{yellow}}{\mathrm{THBF}} + \mathrm{Pb}^{2+} \rightarrow \underset{\text{rose}}{\mathrm{Pb(CMC)_2\text{-}THBF}} + 2\mathrm{Na}^{+}$$

If EDTA (H_2Y^{2-}) was added, $Pb(CMC)_2$-THBF will decompose into THBF, CMC^-, PbY^{2-} and H^+, and the color of solution will change from rose to yellow immediately, the reaction is

$$\underset{\text{rose}}{\mathrm{Pb(CMC)_2 - THBF}} + \mathrm{H_2Y^{2-}} \rightarrow \mathrm{PbY^{2-}} + \underset{\text{yellow}}{2\mathrm{CMC}^{-}} + \mathrm{THBF} + 2\mathrm{H}^{+}$$

If Hg^{2+} ion is present, Hg^{2+} will react with CMC and THBF and form $Hg(CMC)_2$-THBF, which will cause decrease of phosphorescence intensity, the reaction is

$$2\mathrm{CMC}^{-} + \mathrm{THBF} + \mathrm{Hg}^{2+} \rightarrow \mathrm{Hg(CMC)_2\text{-}THBF}$$

According to the facts above, Hg^{2+} ion can be determined by the decrement of phosphorescence intensity.

4. Conclusion

The synthesized $Pb(CMC)_2$-THBF particles can emit intense solid substrate room temperature phosphorescence on filter paper. In the presence of EDTA, many ions such as Cu^{2+}, Hg^{2+}, Ag^{2+} and Pd^{2+} can quench the phosphorescence of $Pb(CMC)_2$-THBF system, so a new method for the determination of trace Cu^{2+}, Hg^{2+}, Ag^{2+} or Pd^{2+} can be established based on quenching of phosphorescence.

Acknowledgements

This work was supported by Chinese National Science Foundation (Grant no. 20175011) and Fujian Province Science Foundation (Grant no. C0110028).

References

[1] D. Myron, Cellulose Chem. Technol. (1997) 349–359.
[2] S.G. Ukai, J. Chromatogr. 8 (1950) 882–886.
[3] X.R. Wen, C.Q. Tu, Chin. J. Anal. Chem. 30 (2002) 89–92.
[4] C.X. Liu, M.Y. Wu, S.J. Wu, Chin. J. Anal. Chem. 30 (2002) 346–348.
[5] A.M. Zhang, Chin. J. Anal. Chem. 26 (1998) 1222–1225.
[6] C.L. Ye, J. Fan, S.L. Feng, Chin. J. Anal. Chem. 28 (2000) 1155–1157.
[7] G.Q. Xi, D.X. Liang, Chin. J. Anal. Chem. 12 (1984) 209.
[8] M.C. Zhou, Y. Jin, H. Bai, Chin. J. Anal. Chem. 14 (1986) 213.
[9] Y.S. Wei, W.J. Jin, Y.L. Yang, C.S. Liu, Chin. J. Anal. Chem. 26 (1998) 515–519.