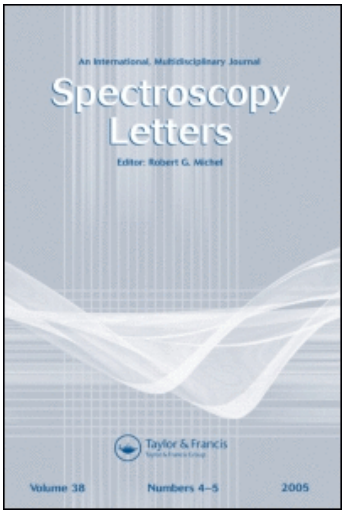

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Determination of Trace Copper by Solid Substrate-Room Temperature Phosphorescence Quenching Method Based on Lead Carboxymethyl Cellulose [$Pb(CMC)_2$] Particles Containing Luminescent Salicyl Fluorones Molecules

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Determination of Trace Copper by Solid Substrate–Room Temperature Phosphorescence Quenching Method Based on Lead Carboxymethyl Cellulose [$Pb(CMC)_2$] Particles Containing Luminescent Salicyl Fluorones Molecules

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Abstract: Luminescent particles of lead carboxymethyl cellulose [$Pb(CMC)_2$] that contain luminescent salicyl fluorones (SAF) {[$Pb(CMC)_2$]-SAF} were synthesized by sol-gel method, using sodium carboxymethyl cellulose (NaCMC) as precursor and Pb^{2+} as precipitator. [$Pb(CMC)_2$]-SAF can emit intense and stable solid substrate–room temperature phosphorescence (SS-RTP) on filter paper. EDTA (ethylenediaminetetraacetic acid) can chelate the Pb^{2+} in [$Pb(CMC)_2$]-SAF, causing it to decompose into aqueous soluble components PbY^{2-}, CMC^{-}, and SAF, and these components can react with Cu^{2+} to form [$Cu(CMC)_2$]-SAF, 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. This method has been applied to the determination of trace copper in human hair and tea samples with satisfactory results.

Keywords: Determination of copper, quenching method, solid substrate–room temperature phosphorescence

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INTRODUCTION

During recent years, many methods for the determination of trace copper have been reported, such as atomic absorption spectra method (limit of detection: 2.0×10^{-11} g mL^{-1}, 4.0×10^{-10} g mL^{-1}, 2.0×10^{-10} g mL^{-1}),[1–3] spectrophotometry (LD: 1.2×10^{-10} g mL^{-1}),[4] ICP method (LD: 9.4×10^{-11} g mL^{-1}),[5] catalytic kinetic discoloring spectrophotometry (LD: 1.92×10^{-9} g mL^{-1}),[6] fluorescence quenching method (LD: 2.2×10^{-10} g mL^{-1}),[7] low-pressure ion chromatography–chemiluminescence method (LD: 1.0×10^{-7} g mL^{-1}),[8] diode array detector–laser induced spectrophotofluorimeter (LD: 5.0×10^{-10} g mL^{-1}),[9] CdS fluorescence probes method (LD: 2.3×10^{-10} g mL^{-1}),[10] photometric analysis using SAF as chromogenic reagent such as salicyl group fluorone and polyglycol caprylpheny ether ($\varepsilon = 1.32 \times 10^5$ L mol^{-1}cm^{-1}),[11] and cetyltrimethylammonium bromide–salicyl fluorone ($\varepsilon = 1.3 \times 10^5$ L mol^{-1} cm^{-1}).[12] Luminescent particles of lead carboxymethyl cellulose [Pb(CMC)$_2$]-SAF that contain salicyl fluorones (SAF) and [Pb(CMC)$_2$] were synthesized by sol-gel method, using sodium carboxymethyl cellulose (NaCMC) as precursor and Pb^{2+} as precipitator. [Pb(CMC)$_2$]-SAF can emit intense and stable solid substrate–room temperature phosphorescence (SS-RTP) on filter paper. EDTA can chelate the Pb^{2+} in [Pb(CMC)$_2$]-SAF, causing it to decompose into aqueous soluble components PbY^{2-}, CMC^-, and SAF, and these components can react with Cu^{2+} to form [Cu(CMC)$_2$]-SAF, causing the quenching of SS-RTP of [Pb(CMC)$_2$]-SAF. Thus, a new method for the determination of trace copper by SS-RTP quenching method was established, with a detection limit of 0.15 fg spot^{-1} (3.75×10^{-13} g mL^{-1}), which is 5.9×10^2 times lower than the lowest detection limit[5] reported before. This sensitive, rapid, and repeatable method has been applied to the determination of trace copper in human hair and tea samples successfully. SS-RTP quenching method based on [Pb(CMC)$_2$]-SAF luminescent particles for the determination of copper has not been reported yet.

MATERIALS AND METHOD

Apparatus and Reagent

Perkin 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, Shanghai, China); 85-1 constant temperature magnetic stirrer (ShenZhen Tian-nan-hai-bei Company, Shenzhen, China); AE240 Electronic analytical balance (Mettler-Toledo Instruments Shanghai Company, Shanghai, China); 0.5-μL flat-head micrometer syringe (Shanghai Medical Laser Instrument Plant, Shanghai, China).

Cu^{2+} primary standard reagent, 1.00 mg mL^{-1} (GSBG 62069-90 8101, $Cu(NO_3)_2$) was diluted to 1.0 μg mL^{-1}, then diluted to 0.010 ng mL^{-1} and 1.00 ng mL^{-1} as working solution before used; 0.1% (w/v) NaCMC solution; 1.0×10^{-4} mol L^{-1} SAF ethanol solution; 5.0×10^{-3} mol L^{-1} Pb^{2+} [$Pb(Ac)_2$] solution; 1% (w/v) EDTA solution; thrice distilled water. All the reagents are A.R. (analytical reagent) grade except that Cu^{2+} is primary standard.

Filter paper (HangZhou Xin-Hua Paper Corporation, Hangzhou, China) was precut into small wafers ($\Phi = 15$ mm), with a ring indentation ($\Phi = 4.0$ 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, Zhejiang, China).

Preparation of $Pb(CMC)_2$-SAF Particle

To 50.00 mL of NaCMC solution, 50.00 mL of SAF solution was added, and then 10.00 mL of Pb^{2+} was added dropwise. Standing for 10 min to precipitate completely, the mixture was centrifuged and washed with water until there was no lead ion (test by sulfuric acid). After dried and being ground, rose powder of [$Pb(CMC)_2$]-SAF was obtained.

Measurement of SS-RTP

[$Pb(CMC)_2$]-SAF 100 mg dry powder was dissolved in 1% EDTA solution, then diluted to 100.0 mL. To a 10-mL cuvette, 1.00 mL of above solution and some copper were added, then diluted to scale graduation line and mixed homogeneously, then stood at room temperature for 10 min. Filter papers ($\Phi = 15$ mm) were immersed in $Pb(Ac)_2$ solution (1.0 mol L^{-1}) for 10 s and then dried at $90 \pm 1^{\circ}C$ 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 for at $90 \pm 1^{\circ}C$ for 2 min. The phosphorescence intensity was directly measured at wavelengths $\lambda_{ex}/\lambda_{em} = 467/637$ nm. The signal of filter paper substrate is defined as the background intensity (Ip_0), the signal of [$Pb(CMC)_2$]-SAF-EDTA system (without Cu^{2+}) is defined as reagent blank intensity (Ip_1), and the signal of [$Pb(CMC)_2$]-SAF-EDTA-Cu^{2+} system is defined as sample intensity for test solution (Ip_2). Then ΔIp ($=Ip_2 - Ip_1$) and the sample/background ratio ($=Ip_2/Ip_0$) were also calculated.

RESULTS AND DISCUSSION

Phosphorescence and Fluorescence Spectra

The phosphorescence and fluorescence spectra of [$Pb(CMC)_2$-SAF], $Pb(CMC)_2$-SAF-Cu^{2+} solution are shown in Fig. 1. Results showed that

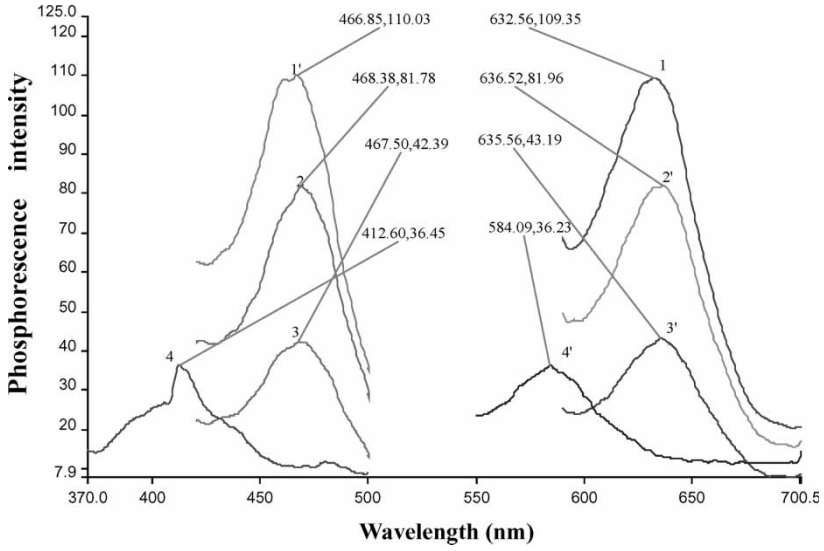

Figure 1. SS-RTP spectra for the [Pb(CMC)$_2$-SAF]-EDTA-Cu^{2+} system: 1,1′, [Pb(CMC)$_2$]-SAF-EDTA; 2,2′, 1,1′ + 0.050 ng Cu^{2+}; 3,3′, 1,1′ + 1.0 ng Cu^{2+}; 4,4′, filter paper.

[Pb(CMC)$_2$]-SAF can emit intense and stable SS-RTP on filter paper at wavelengths $\lambda_{ex}/\lambda_{em} = 467/634$ nm. When [Pb(CMC)$_2$]-SAF was dissolved by EDTA and trace copper was added to the system, the phosphorescence intensity was quenched, and the $\lambda_{ex}/\lambda_{em}$ moved to 468/637 nm, which was chosen as the working wavelength for the determination of trace copper.

Optimum Conditions

Selection of Solid Substrate

For the system containing 1.00 ng mL^{-1} Cu^{2+}, according to the method described above, the SS-RTP spectra of the same test solution were measured at working wavelength $\lambda_{ex}/\lambda_{em} = 468/637$ nm on four kinds of substrates: polyamide membrane (PAM), cellulose acetate membrane (CAM), cellulose nitrate membrane (CNM) and filter paper, respectively. The results showed that the signal/background ratio on filter paper was the highest (Fig. 2), so filter paper was selected as the solid substrate in the following experiment.

The Concentration and Volume of Reagents

For the system containing 1.00 ng mL^{-1} Cu^{2+}, the volumes of different reagents were changed. Results showed that when the volume and

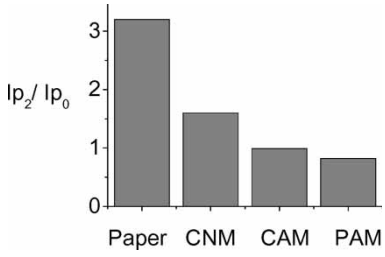

Figure 2. Effects of solid substrate on Ip_2/Ip_0 for system.

concentration were 5.00 mL 0.1% NaCMC, 5.00 mL 1.0×10^{-4} mol L^{-1} SAF alcohol solution, 2.00 mL 5.0×10^{-3} mol L^{-1} Pb^{2+} solution, and 2.00 mL 1.0% EDTA solution, ΔIp reached the maximum.

Heavy Atom Effect

For the system containing 1.00 ng mL^{-1} Cu^{2+}, the effects of heavy atoms such as Pb^{2+}, Ag^{+}, Hg^{2+}, and I^{-} (mol L^{-1}) on signal/background ratio of the system were examined, respectively. The results showed that Ip_2/Ip_0 of Pb^{2+} was the highest, so it was chosen as ion perturber (Fig. 3).

Time and Temperature for Reaction

The experiment showed that under the optimal condition above, when the reaction was carried out at 30°C for 10 min, the ΔIp reached the max and stayed stable (Figs. 4 and 5). In the measurement of phosphorescence, the filter paper was immersed in 1.0 mol L^{-1} $Pb(Ac)_2$ and 2.0 mol L^{-1} HAc-$Pb(Ac)_2$ solution for 10 s, and the paper sheet was dried at 90 ± 1°C for 2 min. Then a ring indentation was made and the sample solution was

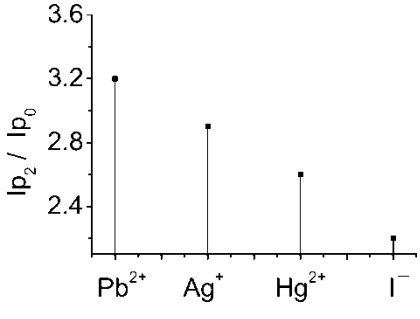

Figure 3. Effects of heavy atoms on Ip_2/Ip_0 for system.

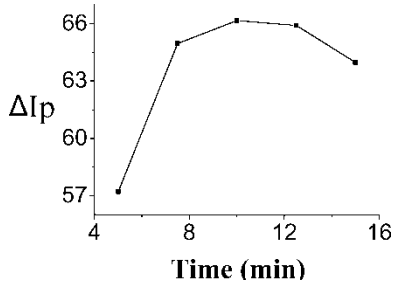

Figure 4. Effect of time on ΔIp for reaction system.

suspended onto the indentation center of the paper sheet. The paper sheet was dried at 90 $\pm$ 1°C for 2 min. The ΔIp reached the max.

Analytical Parameters

When the content of Cu^{2+} is in the range 8.0–40.0 fg spot^{-1} (corresponding concentration of Cu^{2+} is 20.0–100.0 pg mL^{-1}, with a sample volume of 0.4 μL), ΔIp has a good linear correlation with the content of Cu^{2+}. The regression equation ($n = 8$), r, LOD (calculation by 3Sb/k) and RSD% ($n = 11$) are listed in Table 1.

The Lifetime of Phosphorescence

For the sample containing 40.0 fg spot^{-1} Cu^{2+}, the SS-RTP lifetime (τ) obtained by phosphorescence attenuation curve (delay time, 0.1–2.0 ms; gate time, 2.0 ms) is 88.10 ms (Fig. 6). According to the method described in literature,[13] the regression equation of the attenuation curve can be expressed as $\ln Ip = 3.283 - 0.01135t$ ($r = -0.9998$).

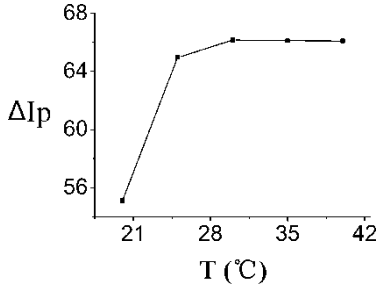

Figure 5. Effect of temperature on ΔIp for reaction system.

Table 1. Comparison of methods

Method	Analytical range	The regression equation	r	LOD	RSD (%)	Method of determination
Proposed	8.0–40.0 (fg spot^{-1})	$\Delta Ip = 24.82 + 1.037$ m Cu^{2+}	0.9992	2.2 (fg spot^{-1})	3.6–4.0	SS-RTP
Method	20.0–100.0 (pg mL^{-1})	fg spot^{-1} ($n = 8$)		0.375 (pg mL^{-1})	($n = 8$)	
Ref. [1]				0.02 (ng mL^{-1})	0.3–5.0	AAS
Ref. [2]				0.4 (ng mL^{-1})	3.6	AAS
Ref. [3]				0.2 (ng mL^{-1})	0.6–2.1	AAS
Ref. [4]				0.12 (ng mL^{-1})	0.6–2.2	Spectrophotometer
Ref. [5]				0.094 (ng mL^{-1})	1.37	ICP
Ref. [6]	0–22 (ng mL^{-1})	$\Delta A = -0.1030\ 89 + 0.1018\ 17$ C (μg L^{-1})	0.9996	1.92 (ng mL^{-1})	1.16	Discoloring spectrophotometry
Ref. [7]	0.0–60.0 (ng mL^{-1})	$F = 74.73 + 0.401$ C Cu^{2+} (μg L^{-1})	−0.9983	0.22 (ng mL^{-1})	1.1	Fluorescence quenching method
Ref. [8]	0.4–60.0 (μg mL^{-1})	$I = -13947 + 3125$ C (mg L^{-1})	0.9955	0.10 (μg mL^{-1})	3.2	Chromatography and chemiluminescence
Ref. [9]	0.5–4.0 (ng mL^{-1})	$\Delta F = 0.09 + 4221.5$ C (μg L^{-1})	0.9986	0.5 (ng mL^{-1})		Laser induced spectrofluorimetry
Ref. [10]	2.0–24.0 (ng mL^{-1})	$\Delta F = -1.20 + 1.54$ C (μg L^{-1})	0.9987	0.5 (ng mL^{-1})		Fluorescence probes

A_3 $\Delta I_p = (Ip_2 - Ip_1)$, and the signal of [Pb(CMC)$_2$]-SAF-EDTA system (without Cu^{2+}) is defined as a reagent blank intensity (Ip_1), and the signal of [Pb(CMC)$_2$]-SAF-EDTA-Cu^{2+} system is defined as sample intensity for test solution (Ip_2).

ΔA $= (A_2 - A_1)$ (A_1 is defined as reagent blank absorbency, and A_2 is defined as sample absorbency for test solution).

F is defined as intensity of fluorescence.

C is defined as column of test solution.

I is defined as intensity of chemiluminescence.

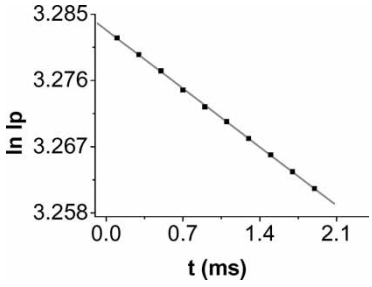

Figure 6. Phosphorescence attenuation curve.

Interference Experiment

For the sample containing 0.10 ng mL^{-1} Cu^{2+}, the allowed concentration (multiple) of coexistent ions ($E_r = \pm 5\%$) were as follows: Na^+, K^+, NH_4^+, F^-, Cl^-, Br^-, S^{2-}, SO_3^{2-}, SO_4^{2-} (5000); Ni^{2+}, Mn^{2+}, Pb^{2+}, CO_3^{2-}, PO_4^{3-}, $C_2O_4^{2-}$(500); NO_2^-, NO_3^-, SCN^- (300); Cd^{2+}, Bi^{3+}, Pb^{2+} (200); Ca^{2+}, Mg^{2+}, Cr^{3+}, Fe^{3+}(150); Co^{2+}, Al^{3+}, Fe^{2+} Zn^{2+} (100).

Analysis of Samples

Pretreatment methods of samples are as follows: for hair sample, 0.2 g ($\pm$0.1 mg) of hair was charred and dried, then charred in a muffle at 500–550°C for 3 h, then it was dissolved and diluted to 50 mL by water. One milliliter of the above solution was taken and diluted to 50 mL; for tea sample, 0.2 g ($\pm$0.1 mg) of tea sample was digested by $HNO_3/HClO_4$ (1 : 3) to colorless and then diluted to 100 mL; 1.0 mL was taken and diluted to 50 mL. The concentration of Cu^{2+} in the sample solutions was determined by the experimental method mentioned above. A recovery experiment was also conducted while adding standard solution. A comparative test with AAS method was also carried out. The results are listed in Table 2.

Table 2. The analytical results of Cu^{2+} in hair and tea samples ($n = 7$)

Samples	Present method (μg/g)	Added (μg/g)	Obtained (μg/g)	Recovery rate (%)	RSD (%)	AAS method (μg/g)
Hair	12.0	1.0	1.01	101	4.2	11.7
Tea	17.2	2.0	0.99	99.0	2.9	16.7

CONCLUSIONS

The synthesized [$Pb(CMC)_2$-SAF] particles by the sol-gel method can emit strong and stable SS-RTP on filter paper. Cu^{2+} can quench the phosphorescence of [$Pb(CMC)_2$-SAF] system, so new methods for the determination of trace Cu^{2+} can be established based on quenching of phosphorescence. This method has high sensitivity, accurate, celerity, and repeatability and is useful for the detection of ultratrace copper.

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