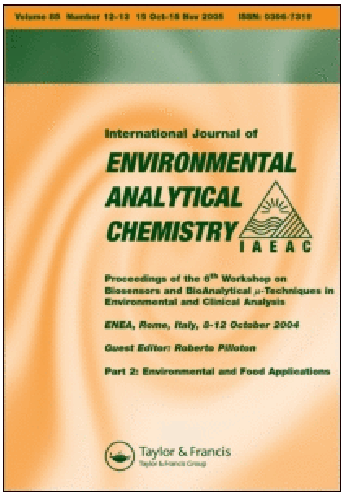

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# Determination of trace mercury by solid substrate-room temperature phosphorimetry based on an ionic associate $[(Rhod.6G)_2]^{2+}\cdot[HgI_4]^{2-}$

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# Determination of trace mercury by solid substrate-room temperature phosphorimetry based on an ionic associate $[(\mathrm{Rhod.6G})_2]^{2+} \cdot [\mathrm{HgI}_4]^{2-}$

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A new solid substrate-room temperature phosphorimetry (SS-RTP) method for the determination of trace mercury has been established. It is based on the fact that in the acidic medium of $H_2SO_4$, an ionic associate will be formed between $[\mathrm{HgI}_4]^{2-}$and Rhodamine 6G (Rhod.6G$^+$) ($[(\mathrm{Rhod.6G})_2]^{2+} \cdot [\mathrm{HgI}_4]^{2-}$). The number of Rhod.6G molecules in the associate is higher than that in Rhod.6G$^+ \cdot \mathrm{I}^-$, and the $\mathrm{Hg}^{2+}$ will induce a heavy atom perturbation effect. Both aspects can cause sharp increase in phosphorescent intensity in a solid substrate. The linear range of this method is 0.80–160.0 fg spot$^{-1}$ (corresponding concentration: 0.002–0.4 ng mL$^{-1}$, sample volume: 0.4 μL spot$^{-1}$) with a limit of detection of 0.15 fg spot$^{-1}$ (corresponding concentration: $3.8 \times 10^{-13}$ g mL$^{-1}$). The regression equation for the working curve is $\Delta I_p = 114.0 + 1.956\, m_{\mathrm{Hg}^{2+}}$ (fg spot$^{-1}$) ($r = 0.9991$. $n = 6$). This method has been successfully applied to the determination of trace mercury(II) in human hair, cigarettes and water. The reaction mechanism for the formation of ionic associate is also discussed.

*Keywords:* Mercury; Rhodamine 6G; Solid substrate-room temperature phosphorimetry

## 1. Introduction

Solid substrate-room temperature phosphorimetry (SS-RTP) has several advantages such as the need for a low sample volume, high sensitivity and simple operation. It has been widely applied in many areas, such as the determination of pesticide carbaryl [1] (LD: 0.1 ng mL$^{-1}$), achromycin [2] (LD: 0.01–1.0 ng spot$^{-1}$), polycyclic aromatic hydrocarbons (such as phenanthrene, pyrene and benzopyrene) [3], furan I-1 (which is the hydrolysis product of pyrenyl-DNA) (LD: 0.14 fmol mg$^{-1}$) [4], luminescent organics [5–7], etc. However, analysing metal ions by room temperature phosphorescence (RTP) is rarely reported, and most of the information is concerned with noble

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metal [8] or lanthanum [9–11] ions. Analysing mercury by RTP property of the ionic associate has not been reported yet. Several methods for the determination of trace mercury have been reported before, such as flow-injection catalytic spectrophotometry (LD: $2.0 \times 10^{-8}\,g\,mL^{-1}$) [12], plasma mass spectrometry (LD: $9.7 \times 10^{-12}\,g\,mL^{-1}$) [13], on-line solid phase extraction-reverse phase liquid chromatographic (LD: $4.0 \times 10^{-12}\,g\,mL^{-1}$) [14], flotation spectrophotometry (LD: $6.8 \times 10^{-9}\,g\,mL^{-1}$) [15], fluorescence spectrometry (LD: $1.0 \times 10^{-11}\,g\,mL^{-1}$) [16], cold-atomic absorption spectrometry (LD: $1.9 \times 10^{-7}\,g\,mL^{-1}$) [17], enzymatic kinetic spectrophotometry (LD: $8.7 \times 10^{-9}\,g\,mL^{-1}$) [18], microwave digestion-hydride generation-atomic fluorescence spectrometry (LD: $5.0 \times 10^{-12}\,g\,mL^{-1}$) [19], etc. The sensitivities of all the methods above are not high; furthermore, for atomic adsorption the operation is complicated, and for fluorescence photometry, the interference of background is serious. Therefore, it is worthwhile finding a method for determination of trace mercury with a high sensitivity, simple operation and light interference.

For the SS-RTP method, the phosphorescent intensity is dependent on the compactness of luminescent molecules on the solid substrate, or the number of luminescent molecules occupying a unit area of solid substrate. Consequently, we can improve the sensitivity of SS-RTP by increasing the number of luminescent molecules per unit area of solid substrate. We found that in the acidic medium of $H_2SO_4$, the ionic associate ($Rhod.6G^+ \cdot I^-$) formed by $I^-$ and $Rhod.6G^+$ can emit strong and stable room temperature phosphorescence on filter paper. If $Hg^{2+}$ is added to the system, it will combine with the $I^-$ ion in the ionic associate $Rhod.6G^+ \cdot I^-$ to form the $[HgI_4]^{2-}$ anion, which can react with $Rhod.6G^+$ to form the ionic associate $[(Rhod.6G)_2]^{2+} \cdot [HgI_4]^{2-}$, resulting in a sharp increase in phosphorescent intensity on solid substrate. Based on this, a new solid substrate-room temperature phosphorimetry with filter paper as solid substrate for determination of trace mercury has been established. This method has been applied to the analysis of trace mercury in hair and cigarette samples with satisfactory results.

## 2. Experimental

### 2.1. *Apparatus and reagents*

For the LS-55 fluorescence spectrophotometer (Perkin Elmer Corporation), the main parameters were: 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 (Medical Laser Instrument Plant, Shanghai, China); 85–1 constant temperature magnetic stirrer (ShenZhen Tiannanhaibei Company); AE240 Electronic analytical balance (Mettler-Toledo Instruments Company); 0.5-μL flat head micrometer syringe (Shanghai Medical Laser Instrument Plant).

For the mercury(II) working solution: mercury(II) primary standard reagent ($1.0\,m\,g\,mL^{-1}$, GSBG 62069–90 (8001), from national steel material test centre) was diluted to $0.01\,ng\,mL^{-1}$ and $1.00\,ng\,mL^{-1}$; rhodamine 6G solution ($1.0 \times 10^{-4}\,mol\,L^{-1}$); iodide anion solution ($1.00\,\mu g\,mL^{-1}$); $H_2SO_4$ ($0.10\,mol\,L^{-1}$); carboxymethylcellulose sodium (CMC) (0.1% w/v); gelatin (5% w/v); polyvinyl alcohol (PVA) (5% w/v); $1.00\,mol\,L^{-1}$ $Pb(Ac)_2$ solution (solvent: $2.0\,mol^{-1}$ HAc); twice distilled water. All the reagents were A.R. grade except the primary standard Hg(II).

Filter paper was pre-cut into small wafers of **Φ** (diameter) = 15 mm, with a ring indentation of **Φ** = 4.0 mm at the centre of each wafer made by a standard pinhole plotter, from Hangzhou XinHua Paper Corporation); acetyl cellulose membrane, nitrocellulose membrane and polyamide membrane were used (Luqiaosijia Biochemical Plastic Plant).

### 2.2. *Method*

To a 25 mL test tube, a certain Hg(II) working solution, 2.00 mL of Rhod.6G solution, 2.00 mL of iodide anion solution and 1.00 mL of $H_2SO_4$ solution were added, and the mixture was then diluted to 25 mL with water, kept at 30°C for 10 min. A blank test (without mercury) was also conducted for comparison. The filter paper was immersed in polyvinyl alcohol solution (5%) for 30 s and dried at $90 \pm 1^\circ C$ for 1 min, then immersed in $Pb(Ac)_2$ solution ($1.0\,mol\,L^{-1}$) for 10 s and dried at $90 \pm 1^\circ C$ for 2 min. A drop of sample solution (0.4 µL) was suspended onto the indentation centre of filter paper wafer using a 0.5 µL micrometer syringe, and then the filter paper was dried at $90 \pm 1^\circ C$ for 2 min. The phosphorescent intensity was measured directly at $\lambda_{ex}^{max}/\lambda_{em}^{max} = 485/649$ nm. The signal without addition of reagents (signal of substrate) is defined as background intensity ($I_{p0}$), the signal of the Rhod.6G-$H_2SO_4$-$I^-$ system (without $Hg^{2+}$) is defined as the reagent blank intensity ($I_{p1}$), and the signal of the Rhod.6G–$Hg^{2+}$–$H_2SO_4$–$I^-$ system is defined as the sample intensity ($I_p$) for the test solution. Then, $\Delta I_p (= I_p - I_{p1})$ and the sample/background ratio ($= I_p/I_{p0}$) were calculated.

### 2.3. *Sample analysis*

A hair sample ($500 \pm 0.1$ mg) was washed and dried, then digested using a mixture of 2 mL of $HClO_4$ (70%, V/V) and 10 mL of $HNO_3$ (65%, V/V). The mixed solution was then heated to nearly dryness and the residue dissolved and diluted to 50 mL with water. A HongMei cigarette ($200 \pm 0.1$ mg) was treated according to the method in the literature [20], diluted to 250 mL with water, and then mixed homogeneously by shaking.

The water sample (1000 mL of running water from Zhangzhou Running Water Plant) was enriched to 20 mL, the pH adjusted to 2.5, then diluted to 200 mL with water; 200 mL of waste water (Zhangzhou Chemicals Plant) was added to a beaker, and then 4.00 mL of $3.0\,mol\,L^{-1}$ $H_2SO_4$ and 0.10 mL $1.0\,mol\,L^{-1}$ $KMnO_4$ were added. The mixed solution was digested for 1 h at a low temperature, $0.1\,mol\,L^{-1}$ hydroxylamine hydrochloride was added dropwise to reduce the excessive $KMnO_4$ and the mixture was then diluted with water. Next, a certain amount of NaOH was added until the pH was 2.5. The solution was diluted to 100.0 mL and then mixed by shaking.

## 3. Results and discussion

### 3.1. *Phosphorescence spectra and fluorescence spectra*

The solid substrate-room temperature phosphorescence spectra of the sample and the blank reagent were both scanned according to the experimental method (figure 1).

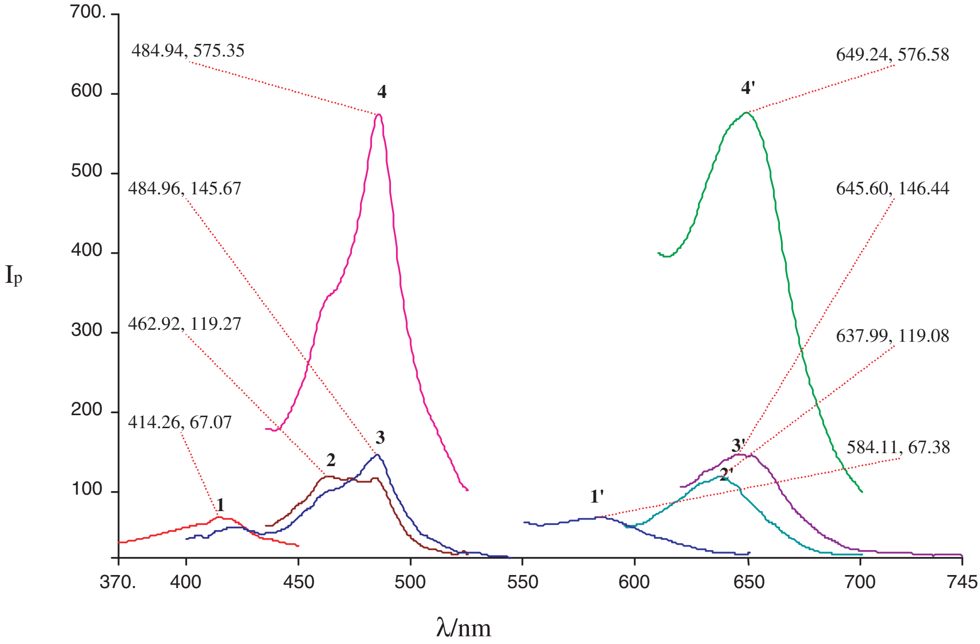

Figure 1. SS-RTP spectra (left, excitation spectra; right, emission spectra) of the Rhod.6G–$Hg^{2+}$–$H_2SO_4$–$I^-$ system. 1.1′: paper; 2.2′: 2.00 mL of Rhod.6G + 1.00 mL of $H_2SO_4$; 3.3′ : 2.2′ + 2.00 mL of $I^-$; 4.4′ : 3.3′ + 10.00 ng $Hg^{2+}$.

The results indicate that $Rhod.6G^+$(red) can emit room temperature phosphorescence on filter paper, the $\lambda_{ex}^{max}/\lambda_{em}^{max}$ is 463/638 nm, and the phosphorescent intensity ($I_p$) is 119.08. If iodide anion ($I^-$) is present, an ionic associate $Rhod.6G^+ \cdot I^-$ (yellow) will be formed by $I^-$ and $Rhod.6G^+$ with a red shift for 8 nm, and the phosphorescent intensity will also increase. The $\lambda_{ex}^{max}/\lambda_{em}^{max}$ is 485/646 nm and the $I_p$ value is 146.44. If $Hg^{2+}$ is added to the system, it will acquire $I^-$ in the ionic associate $Rhod.6G^+ \cdot I^-$ and form the yellow precipitate of $HgI_2$, causing the ionic associate $Rhod.6G^+ \cdot I^-$ to dissociate. However, the $HgI_2$ precipitate can be dissolved in excess $I^-$ and form the coordination anion $[HgI_4]^{2-}$. $[HgI_4]^{2-}$ can combine with $Rhod.6G^+$ to form a new ionic associate $[(Rhod.6G)_2]^{2+} \cdot [HgI_4]^{2-}$ (orange), which causes a sharp increase in the system's phosphorescent intensity. The $\lambda_{ex}^{max}/\lambda_{em}^{max}$ is 485/649 nm, and the $I_p$ is 576.58 (figure 1). The $\lambda_{ex}^{max}/\lambda_{em}^{max}$ is 529/551 nm, and the phosphorescent intensity ($I_p$) is 364.33. For $[(Rhod.\ G)_2]^{2+} \cdot [HgI_4]^{2-}$, the $\lambda_{ex}^{max}/\lambda_{em}^{max}$ is 533/583 nm, and the $I_f$ is 733.87, with an increasing tendency of fluorescent intensity similar to that of phosphorescent intensity, but the $\lambda_{ex}^{max}/\lambda_{em}^{max}$ are different (figure 2). Thus, $\lambda_{ex}^{max}/\lambda_{em}^{max} = 485/649$ nm was chosen as the working wavelength.

### 3.2. *Optimum measuring conditions*

**3.2.1. Concentration and volume of reagents.** For the system containing 10.0 ng of $Hg^{2+}$, the volume and concentration of the reagents were optimized, respectively. The results showed that when the system contained 2.00 mL of $1.0 \times 10^{-4}$ mol $L^{-1}$

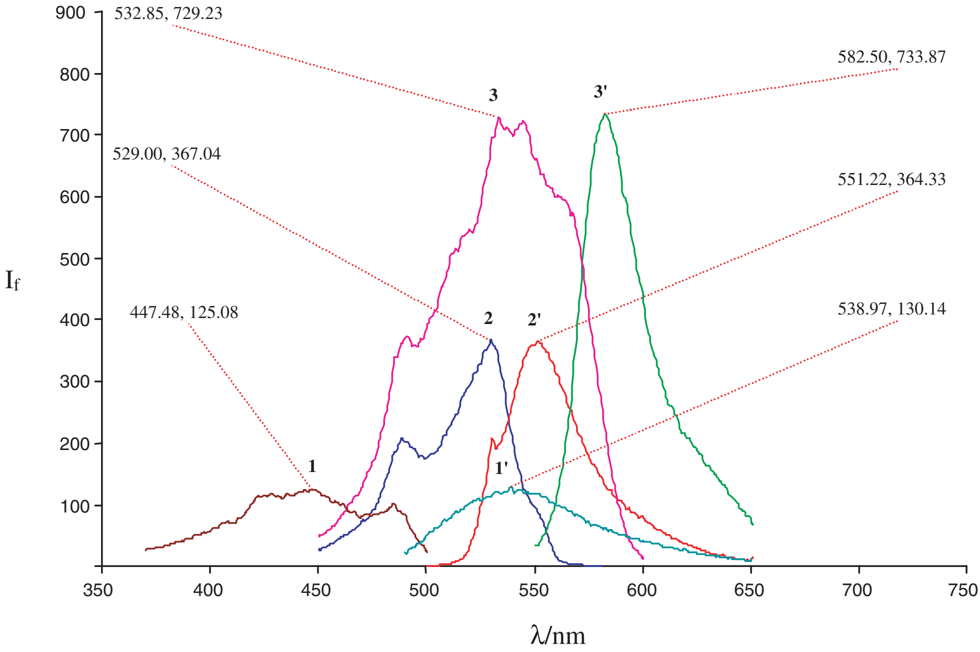

Figure 2. Fluorescence spectra (left, excitation spectra; right, emission spectra) of Rhod.6G–$Hg^{2+}$–$H_2SO_4$–$I^-$ system (ex slit 10 nm, em slit 2.5 nm). 1.1′ : 2.00 mL of Rhod.6G + 1.00 mL of $H_2SO_4$; 2.2′ : 1.1′ + 2.00 mL of $I^-$; 3.3′ : 2.2′ + 10.00 ng of $Hg^{2+}$.

Rhod.6G solution, 2.00 mL of 1.00 μg $mL^{-1}$ $I^-$ solution and 1.00 mL of 0.10 mol $L^{-1}$ $H_2SO_4$, the $\Delta I_p$ of the system reached the maximum and remained stable.

**3.2.2. Heavy atom effect.** The effects of different heavy atoms (1.0 mol $L^{-1}$) on the $\Delta I_p$ of the system were examined, respectively. The results showed that the $\Delta I_p$ values were 430.14, 267.83 and 309.69 for $Pb^{2+}$, $Cu^{2+}$ and $Ag^+$. The $Pb^{2+}$ had the main effect on $\Delta I_p$. The effects of 0.25, 0.50, 0.75, 1.0 and 1.25 mol $L^{-1}$ $Pb^{2+}$ on $\Delta I_p$ of system were also examined. The results indicated that when $C_{Pb}^{2+} = 1.0$ mol $L^{-1}$ for the reaction system, the $\Delta I_p$ of this system reached the maximum (figure 3).

**3.2.3. Acidity.** For the system containing 10.0 ng of $Hg^{2+}$, the effects of different acidities on the system were examined. The results showed that the system was stable when $2.0 < pH < 3.0$. The $\Delta I_p$ reached the maximum and remained stable when 1.00 mL of 0.1 mol $L^{-1}$ $H_2SO_4$ was used to adjust the acidity to $pH = 2.50$ (figure 4).

**3.2.4. Time and temperature for the reaction.** For the system containing 10.0 ng of $Hg^{2+}$, the time and temperature for reaction were changed, respectively. The results showed that when the time was 10 min, and the temperature was 30°C, the $\Delta I_p$ reached the maximum (figures 5 and 6).

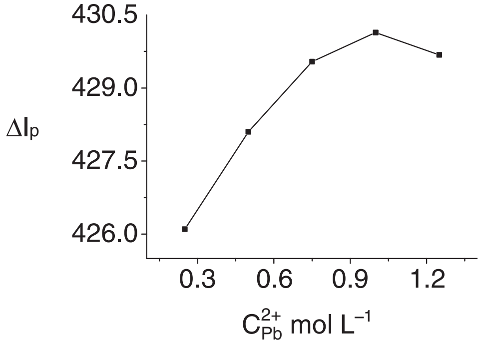

Figure 3. Effect of $C_{Pb}^{2+}$ on $\Delta I_p$.

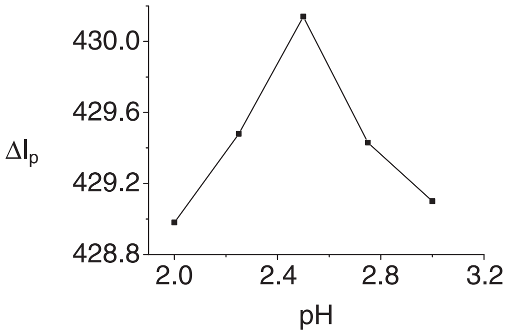

Figure 4. Effect of pH on $\Delta I_p$.

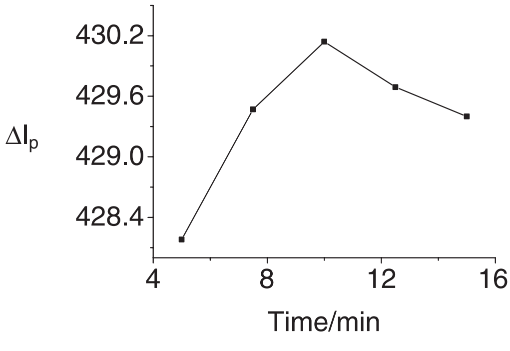

Figure 5. Effect of time on $\Delta I_p$.

**3.2.5. Time and temperature for drying.** The experimental results indicated that when the drying temperature was 90 ± 1°C, and the time for drying was 2 min, the $\Delta I_p$ of the system reached the maximum. When the filter paper was modified with PVA, the drying time was 1 min.

**3.2.6. Selecting substrate.** For the system of 10.00 ng mL$^{-1}$ Hg$^{2+}$, according to the method described above, the SS-RTP spectra of the same reaction solution and the

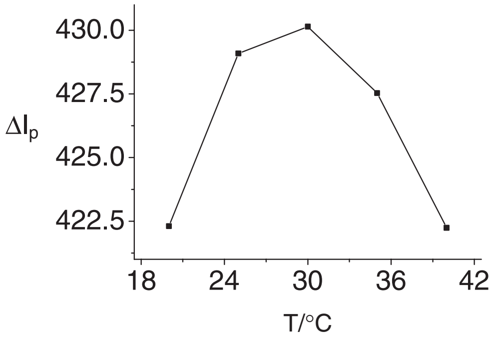

Figure 6. Effect of temperature on $\Delta I_p$.

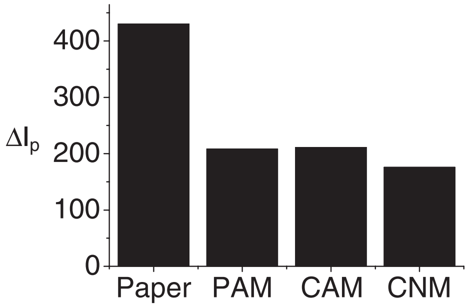

Figure 7. Effect of solid substrate on $\Delta I_p$.

reagent blank were measured at the working wavelength ($\lambda_{ex}^{max}/\lambda_{em}^{max} = 485/649\,nm$) on four kinds of substrates. These were polyamide membrane, cellulose acetate membrane, cellulose nitrate membrane and quantitative filter paper, respectively. The results showed that three kinds of substrates, except the filter paper, were unsuitable for SS-RTP determination owing to the weak signal intensity for analysis applications. The $\Delta I_p$ on filter paper was the highest (figure 7), so this was selected as the substrate in the following experiment.

**3.2.7. Modification of the filter paper.** For the system of $10.00\,ng\,mL^{-1}$ $Hg^{2+}$, the filter paper was modified by CMC (0.1% w/v), gelatin (5% w/v) and PVA (5% w/v), respectively. Then, their effects on the $\Delta I_p$ of the system were examined, respectively (figure 8). The results showed that the effect of PVA on $\Delta I_p$ was the greatest, so the PVA was chosen in our experiment. Probably, the hardening effect of PVA on the filter paper is the most significant.

### 3.3. *Component of the ionic associate*

The component of the ionic associate was determined by the equimolar ratio continuous variation method and the molar ratio method. The results showed that the ratio for $Rhod.6G^+ : I^-$ is 1 : 1, so the component is $Rhod.6G^+ \cdot I^-$. The ratio for $Hg^{2+} : I^- : Rhod.6G^+$ is 1 : 4 : 2, so the component can be expressed as $[(Rhod.6G)_2]^{2+} \cdot [HgI_4]^{2-}$.

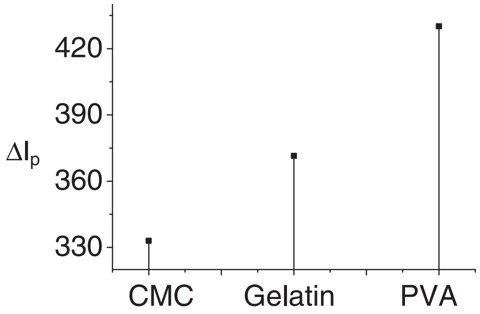

Figure 8. Effect of surface modification reagents on $\Delta I_p$.

### 3.4. *Working curve*

Under optimal conditions, the linear range of $Hg^{2+}$ is 0.80–160.0 fg spot$^{-1}$ (corresponding concentration: 0.0020–0.40 ng mL$^{-1}$, sample volume: 0.4 µL). The regression equation can be expressed as $\Delta I_p = 114.0 + 1.956m_{Hg^{2+}}$ (fg spot$^{-1}$) ($n = 6, r = 0.9991$). If the $3Sb/K$ ($n = 11$) is defined as the detection limit, the detection limit is 0.15 fg spot$^{-1}$ (with a corresponding concentration is $3.8 \times 10^{-13}$ g mL$^{-1}$). The system containing 0.002 ng mL$^{-1}$ and 0.40 ng mL$^{-1}$ of $Hg^{2+}$ was determined for 11 times, and the RSD values were 4.2% and 3.0% ($n = 11$), respectively. The results indicated that this method had a good repeatability.

### 3.5. *Interference of coexistent ions*

When the relative error is ±5%, for the system containing 10.0 ng of $Hg^{2+}$, the allowable concentrations (multiple) of coexistent ions are as follows: $NH_4^+$, $Na^+$, $K^+$, $Mg^{2+}$, $Cl^-$ and $Br^-$(1500); $Ca^{2+}$, $Sr^{2+}$, $Zn^{2+}$, $Ba^{2+}$, $SO_3^{2-}$ and $CO_3^{2-}$ (1300); $SiO_3^{2-}$, $Ti^{4+}$, $C_2O_4^{2-}$, $SO_4^{2-}$ and $PO_4^{3-}$ (1000); $Cr^{3+}$, $Ni^{2+}$, $Cd^{2+}$, $SCN^-$ and $Al^{3+}$ (500); $S_2O_3^{2-}$ (250); $Fe^{2+}$, $Co^{2+}$, $Sn^{4+}$, $NO_3^-$ and $Cu^{2+}$ (100). If 0.5 mL of EDTA (5%, w/v) is added, $Fe^{3+}$, $Sb^{2+}$ and $Bi^{3+}$ (100) do not interfere with the system.

### 3.6. *Phosphorescence lifetime*

For the system containing 160 fg spot$^{-1}$ of $Hg^{2+}$, the phosphorescence lifetime ($\tau$) was measured by the phosphorescence decay method (delay time: 0.1–2.0 ms; gate time: 2.0 ms). The phosphorescence attenuation curve [21] is shown in figure 9. The regression equation for the attenuation curve is $\ln I_p = 3.329 - 0.00512t$, with a correlation coefficient ($r$) of 0.9983. According to the definition of phosphorescent lifetime, a $\tau_P$ value of 195.3 ms was obtained.

### 3.7. *Reaction mechanism for the formation of ionic associates*

In the $H_2SO_4$ medium (0.10 mol L$^{-1}$), Rhod.6G exists in the form of Rhod.6G$^+$ [22]:

$$\text{Rhod.6G} + H^+ \rightarrow \text{Rhod.6G}^+ \text{ (red)}$$

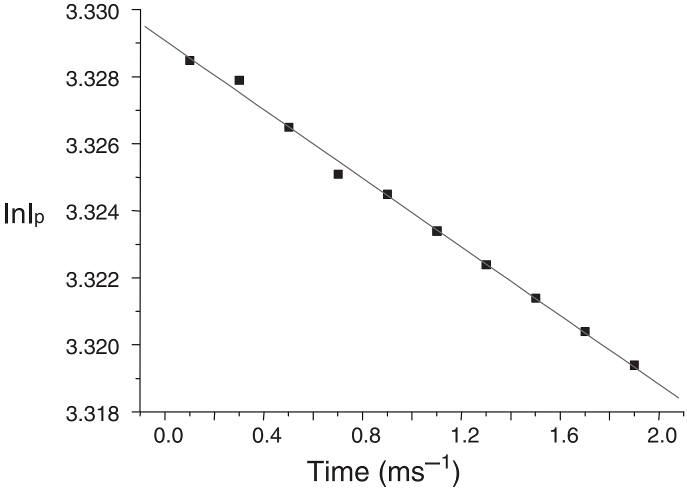

Figure 9. Phosphorescence attenuation curve.

If $I^-$ is added to the system, it will react with Rhod.6G$^+$ and form an ionic associate Rhod.6G$^+ \cdot I^-$, which can emit strong and stable room temperature phosphorescence on filter paper. The reaction can be expressed as:

$$\mathrm{Rhod.6G^+ + I^- \rightarrow Rhod.6G^+ \cdot I^-}\ \text{(yellow)}$$

If $Hg^{2+}$ is added, it will accumulate $I^-$ in Rhod.6G$^+ \cdot I^-$ and form the red precipitate of $HgI_2$, causing dissociation of the ionic associate Rhod.6G$^+ \cdot I^-$:

$$\mathrm{Hg^{2+} + 2Rhod.6G^+ \cdot I^- \rightarrow HgI_2 + 2Rhod.6G^+}$$

However, the $HgI_2$ precipitate can be dissolved in excess $I^-$ [23] and form a coordination anion $[HgI_4]^{2-}$:

$$\mathrm{Hg^{2+} + 2I^- \rightleftharpoons HgI_2 + 2I^- \rightleftharpoons [HgI_4]^{2-}}$$

$[HgI_4]^{2-}$ will combine with Rhod.6G$^+$ and form a new ionic associate $[(\mathrm{Rhod.6G})_2]^{2+} \cdot [HgI_4]^{2-}$:

$$\mathrm{2Rhod.6G^+ + [HgI_4]^{2-} \rightarrow [(Rhod.6G)_2]^{2+} \cdot [HgI_4]^{2-}}\ \text{(orange)}$$

For the SS-RTP method, the phosphorescent intensity depends on the number of luminescent molecules occupied on a unit area of solid substrate. The number of Rhod.6G molecules contained in $[(\mathrm{Rhod.6G})_2]^{2+} \cdot [HgI_4]^{2-}$ is twice that in the Rhod.6G$^+ \cdot I^-$. Moreover, the former contains the coordination anion $[HgI_4]^{2-}$, which includes heavy atom mercury that can induce a micro-interference effect. These factors result in a sharp increase in the phosphorescent intensity on solid substrate. This phenomenon is applied to the possibility for the determination

Table 1. Analytical results for trace mercury in samples.

| Sample | Present method | Added | Obtained | Recovery (%) | RSD (%) | Dithizone method |
|---|---|---|---|---|---|---|
| Hair ($\mu g\,g^{-1}$) | 0.35 | 0.40 | 0.41 | 102.5 | 2.9 | 0.36 |
| Cigarette ($\mu g\,g^{-1}$) | 6.6 | 0.70 | 0.72 | 102.9 | 3.7 | 6.4 |
| Tap water ($\mu g\,L^{-1}$) | 0.006 | 0.006 | 0.006 | 100.0 | 2.8 | 0.006 |
| Waste water ($\mu g\,L^{-1}$) | 0.30 | 0.30 | 0.31 | 103.3 | 3.9 | 0.29 |

of trace mercury by solid substrate-room temperature phosphorimetry based on an ionic associate.

### 3.8. *Analytical result*

The contents of $Hg^{2+}$ in hair and water samples were determined according to the experimental method. A standard addition recovery experiment was also conducted. The results are listed in table 1. According to these, the present method is accurate and reliable, as it provides results comparable with those found with the conventional dithizone method [24].

## 4. Conclusion

The ionic associate formed by metallic coordination anion and basic xanthydrol dye cation can increase the compactness of luminescent molecules, and the included heavy atoms may induce a micro-interference effect. Based on these facts, a new solid substrate-room temperature phosphorimetry method for the determination of a series of trace metals with high sensitivity can be established. This method is not only applied to determine mercury in biological and environmental samples, but is also a new way of increasing the sensitivity of the SS-RTP method.

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