

# Electrochemical behaviors of metal on ionic-liquid-modified carbon paste electrode and its analytical application

Wei Sun · Qiang Jiang · Kui Jiao

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**Abstract** The electrochemical behaviors of metal on an ionic liquid *N*-butylpyridinium hexafluorophosphate modified carbon paste electrode (IL-CPE) were studied in this paper. The results indicated that a pair of well-defined quasi-reversible redox peaks of metal appeared with the decrease of overpotential and the increase of redox peak current, which was the characteristics of electrocatalytic oxidation. The electrocatalytic mechanism was discussed and the electrochemical parameters were calculated with results of the charge-transfer coefficient ( $\alpha$ ) as 0.45, the electrode reaction rate constant ( $k_s$ ) as  $4.02 \times 10^{-3} \text{ s}^{-1}$ , and the diffusion coefficient ( $D$ ) as  $6.35 \times 10^{-5} \text{ cm}^2/\text{s}$ . Under the optimal conditions, the anodic peak current was linear with the metal concentration in the range of  $5.0 \times 10^{-6} \sim 1.0 \times 10^{-3} \text{ mol/L}$  ( $n=11$ ,  $\gamma=0.994$ ) and the detection limit was estimated as  $2.33 \times 10^{-6} \text{ mol/L}$  ( $3\sigma$ ). The proposed method was successfully applied to determination of metal content in synthetic samples and photographic solutions.

**Keywords** Ionic liquid · Carbon paste electrode · Metal · Electrocatalysis · *N*-butylpyridinium hexafluorophosphate

## Introduction

Ionic liquids (ILs) have attracted great interests in recent years for their specific properties such as negligible vapor pressure, wide potential windows, good ionic conductivity, and extraction and catalytic ability [1–3]. In the field of

electroanalysis, ILs can be used as not only the supporting electrolyte but also the modifier for the working electrode. Rozniecka and Shul et al. [4–6] studied the ion-transfer mechanism occurring across ILs–aqueous solution interface with different working electrodes. Wadhawan et al. [7] applied a microdroplet and thin-film deposits of IL ( $\text{MDIM}^+\text{BF}_4^-$ ) on the electrode surface and investigated its unusual partitioning and diffusion effect to  $\text{Fe}(\text{CN})_6^{4-/3-}$ . Wei and Ivaska [8] reviewed the recent applications of ILs in the electrochemical biosensor. Several groups had incorporated ILs with some conventional matrices such as Nafion [9] and chitosan [10] or nanomaterials such as carbon nanomaterials [11] to get unique composite materials for the modification of electrode and further used for different electroactive substance detection. Zhu et al. [12] fabricated a carbon nanotube and 1-octyl-3-methylimidazolium hexafluorophosphate gel modified electrode for the selective detection of dopamine. Li et al. [13] fabricated single-walled carbon nanotubes (SWCNT) and IL composite gel electrode for the electrochemical detection of nitric oxide. Zhao et al. [14] also used SWCNT-IL-gel-modified electrode for the *p*-nitroaniline detection. Direct electrochemistry of redox proteins had also been investigated on different IL composite material modified electrodes [15–18]. Due to the higher conductivity of IL, different kinds of ILs had been applied as the binder to make the modified carbon paste electrode (CPE). Liu et al. [19] reported the ionic-liquid-type carbon paste electrode and its polyoxometalate-modified properties. Maleki et al. [20–23] developed an ionic-liquid-modified carbon paste electrode with ILs of 1-octylpyridinium hexafluorophosphate as binder and further used it for the detection of some electroactive molecules. Sun et al. [24–26] also applied the ionic-liquid-modified CPE for the investigation of the direct electrochemistry of hemoglobin and ssDNA [27].

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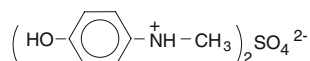
Metol (*p*-methylaminophenol sulfate, molecular structure shown in Fig. 1) is a commonly used monochrome photographic chemical and has attracted much attention due to its toxicity and persistence. It is a main developing agent used in photographic developers. In its pure form, it is a solid rather light-sensitive chemical which is the half sulfate (hemisulfate) salt of *N*-methyl-*p*-aminophenol. Metol is an excellent developing agent for most continuous tone developer applications, and it has been widely used in published developer formulas as well as commercial products. Because it has been in use for this purpose for over 100 years and often by amateur photographers, there is a wide body of evidence about the health problems that contact with metol can cause. Different kinds of methods such as photolysis [28], ceric oxidimetry [29], Fenton reagent [30], mass-chromatogram spectrum [31], spectrophotometry [32], and electrochemical method [33] have been reported for the determination of metol. Among these methods, some need a long time to perform the experiments and some have low precision because of their unavoidable system error. For example, the spectrophotometry is time-consuming with developing reaction. The ceric oxidimetry often gives much higher results because ethyl acetate and water are difficult to separate completely and form systematic positive error. Therefore, it is important to establish a simple, accurate, and highly sensitive method for metol determination. Wang et al. [34] employed an L-cysteine self-assembled monolayer-modified gold electrode for the determination of metol. Li et al. [35] established a direct electrochemical method based on the multiwall carbon nanotube modified glassy carbon electrode to detect the metol.

In this paper, an ionic liquid *N*-butylpyridinium hexafluorophosphate (BPPF<sub>6</sub>) modified carbon paste electrode was used for the investigation of the electrochemical behaviors of metol for the first time. The ionic-liquid-modified carbon paste electrode (IL-CPE) showed good electrocatalytic activity to the oxidation of metol in the Britton-Robinson (B-R) buffer solution, which was attributed to the presence of IL in the modified electrode. The electrochemical behaviors of metol were carefully studied on the IL-CPE and further a sensitive voltammetric method for metol determination was developed.

## Experimental

### Chemicals

Metol (Shanghai Chemical Reagent Station), *N*-butylpyridinium hexafluorophosphate (Hangzhou Kemer Chemical Limited



**Fig. 1** The molecular structure of metol

Company) and graphite powder (average particle size 30 μm, Shanghai Colloid Chemical Plant) were used as received. A 0.2-mol/L solution of B-R buffer was used as the supporting electrolyte. All the chemicals were of analytical reagent grade and used without further purification; the solutions were prepared by doubly distilled water.

### Apparatus

All the electrochemical measurements were carried out on an LK 98A electrochemical workstation (Tianjin Lanlike Chemistry and Electron High Technology Company, China). A traditional three-electrode system was used including a homemade ionic-liquid-modified carbon paste electrode as working electrode ( $\Phi=4.0$  mm), a saturated calomel reference electrode (SCE), and a platinum wire auxiliary electrode. All the experiments were performed at  $20 \pm 1^\circ\text{C}$ .

### Electrode preparation

The traditional carbon paste electrode (CPE) was prepared by hand-mixing of graphite powder with paraffin oil at a ratio of 70:30 (*w/w*) in an agate mortar. The procedure for the preparation of IL-CPE was carried out according to [36], which was made of graphite powder and BPPF<sub>6</sub> at a ratio of 3:1 (*w/w*). The surface of IL-CPE was polished on a piece of weighing paper to get a mirror-like surface just before use.

### Electrochemical measurements

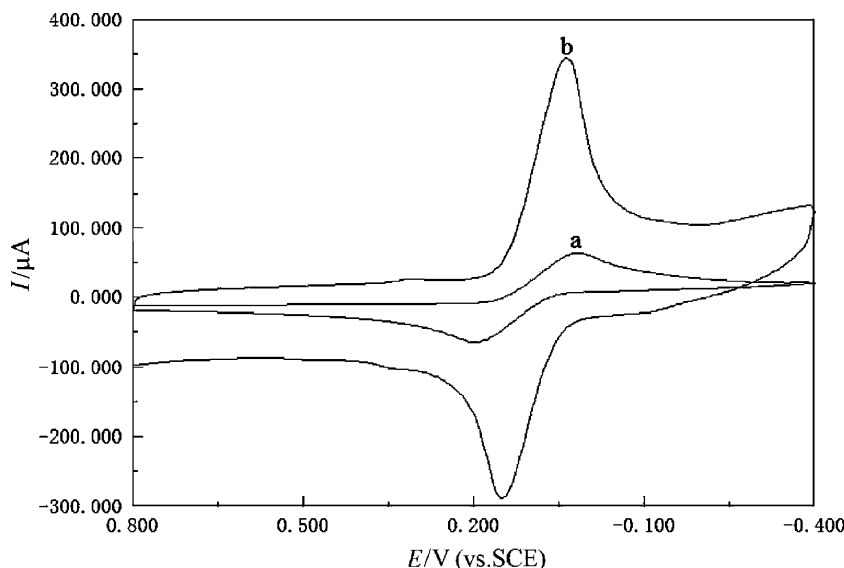
The three-electrode system was immersed in a 10-mL electrochemical cell containing metol or sample and 0.2 mol/L pH 6.5 B-R buffer. Then the cyclic voltammograms were recorded in the potential range from 0.8 to  $-0.4$  V at the scan rate of 0.10 V/s.

## Results and discussion

### Electrochemical behaviors of metol on CILE

Figure 2 showed the cyclic voltammograms of  $5.0 \times 10^{-4}$  mol/L metol on IL-CPE and CPE in 0.2 mol/L pH 6.5 B-R buffer. A pair of redox peaks appeared on the CPE (curve a) with the anodic ( $E_{\text{pa}}$ ) and the cathodic ( $E_{\text{pc}}$ ) peak potential located at 0.192 and 0.020 V (vs. SCE), respectively. The anodic ( $I_{\text{pa}}$ ) and the cathodic ( $I_{\text{pc}}$ ) peak current were gotten as  $-70.167$  and  $74.749$  μA, respectively. The peak-to-peak separation ( $\Delta E_{\text{p}}$ ) was calculated as 0.172 V and the ratio of redox peak current ( $I_{\text{pa}}/I_{\text{pc}}$ ) as 0.94, which were the characteristics of quasi-reversible electrode

**Fig. 2** Cyclic voltammograms of  $5.0 \times 10^{-4}$  mol/L metal at CPE (a) and IL-CPE (b) with the scan rate as 0.10 V/s



process. While on the IL-CPE a pair of well-defined redox peaks was obtained with the greatly increased redox peak currents (curve b). The anodic ( $E_{pa}$ ) and the cathodic ( $E_{pc}$ ) peak potential were gotten at 0.140 and 0.056 V (vs. SCE) with the peak-to-peak separation ( $\Delta E_p$ ) as 0.084 V. The peak current increased for about fourfold larger than that on the CPE. It is well-known that the decrease of overpotential and the increase of redox peak current are the typical results of electrocatalytic behavior. The experimental results indicated that IL-CPE showed good electrocatalytic ability to the electrochemical reaction of metal, which was due to the presence of IL in the carbon paste. Based on the recent reports [37, 38], in the IL-CPE, ionic liquid could adhere to the graphite powder homogeneously; a layer of IL was formed on the surface of graphite powder and IL was also filled into the void space between the graphite powder. The conductivity of the IL-CPE was greatly improved by the contributions of the electronic conductivity of graphite powder and the ionic conductivity of ionic liquid at the same time. Due to the specific physical and chemical properties of IL, the presence of IL in the electrode acted as a suitable charge-transfer bridge to facilitate the electron transfer rate and exhibited enhanced electrocatalytic results.

**Influence of scan rate**

The influence of the scan rate ( $\nu$ ) on the cyclic voltammetric response was investigated with the results shown in Fig. 3. At the lower scan rate range from 10 to 40 mV/s, the relationship of redox peak currents with scan rate were constructed with the equations as  $I_{pa} (\mu\text{A}) = -4,501.7\nu (\text{V/s}) - 7.5$  ( $n=7, \gamma=0.997$ ) and  $I_{pc} (\mu\text{A}) = 5,952.3\nu (\text{V/s}) + 4.0$  ( $n=7, \gamma=0.997$ ), which demonstrated that the electrode

reaction of metal was an adsorption-controlled process. Since the IL had the preconcentration ability, the IL on the surface of IL-CPE can adsorb a certain amount of metal on the electrode surface. At the scan rate from 40 to 500 mV/s, the redox peak current of metal was proportional to the square root of the scan rate ( $\nu^{1/2}$ ) with the linear regression equations as  $I_{pa} (\mu\text{A}) = -1,409.5\nu^{1/2} (\text{V/s}) + 144.1$  ( $n=15, \gamma=0.997$ ) and  $I_{pc} (\mu\text{A}) = 1,430.5\nu^{1/2} (\text{V/s}) - 83.2$  ( $n=15, \gamma=0.996$ ), which demonstrated that the electrode reaction of metal was a diffusion-controlled process at higher scan rate. The results may attribute to the high conductivity of IL-CPE and the diffusion of metal in the IL-rich surface.

With the increase of the scan rate, the redox peak potentials also shifted with the anodic peak potential to a positive direction and the cathodic peak potential to a negative direction. The peak-to-peak separation also increased, which indicated that the electron transfer rate was not very fast, according to the following equations [39]:

$$E_{pa} = E^{0'} + m [0.78 + \ln(D^{1/2}k_s^{-1}) - 0.5 \ln m] + \frac{m}{2} \ln \nu,$$

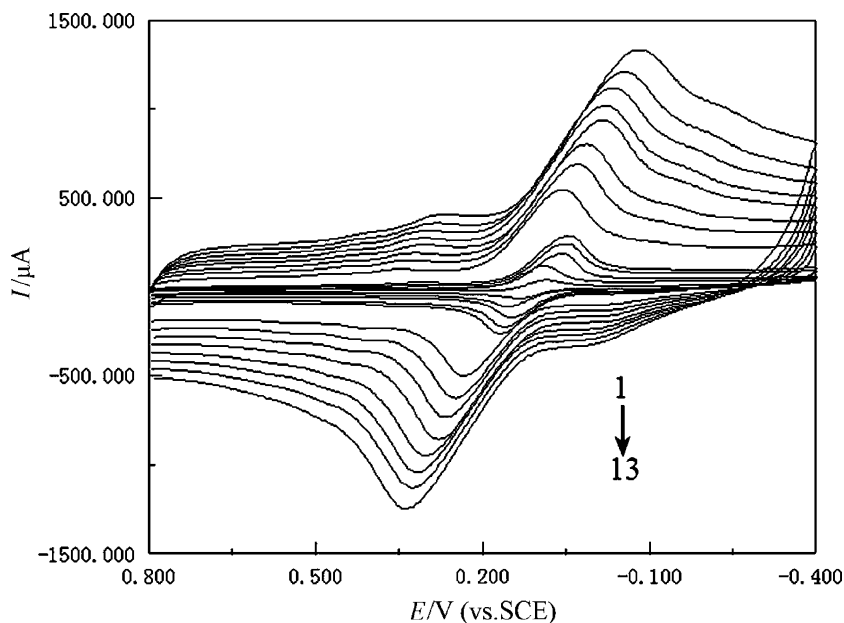
where  $m = \frac{RT}{(1-\alpha)n_a F}$

$$E_{pc} = E^{0'} - m' [0.78 + \ln(D^{1/2}k_s^{-1}) - 0.5 \ln m'] - \frac{m'}{2} \ln \nu,$$

where  $m' = \frac{RT}{\alpha n_a F}$

At higher scan rate, the redox peak potential ( $E_p$ ) exhibited a good linear relationship with  $\ln \nu$  with the regression equations as  $E_{pa} (\text{V}) = 0.0225 \ln \nu + 0.270$  ( $n=8, \gamma=0.991$ ) and  $E_{pc} (\text{V}) = -0.0271 \ln \nu - 0.0241$  ( $n=8, \gamma=0.991$ ). So the values of the charge-transfer coefficient ( $\alpha$ ) and the electrode

**Fig. 3** Cyclic voltammograms of  $5.0 \times 10^{-4}$  mol/L metal at IL-CPE with different scan rates (1–13 0.01, 0.02, 0.03, 0.06, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, 0.40, 0.45, 0.50 V/s)



reaction standard rate constant ( $k_s$ ) were calculated as 0.45 and  $4.02 \times 10^{-3} \text{ s}^{-1}$ .

#### Chronocoulometry

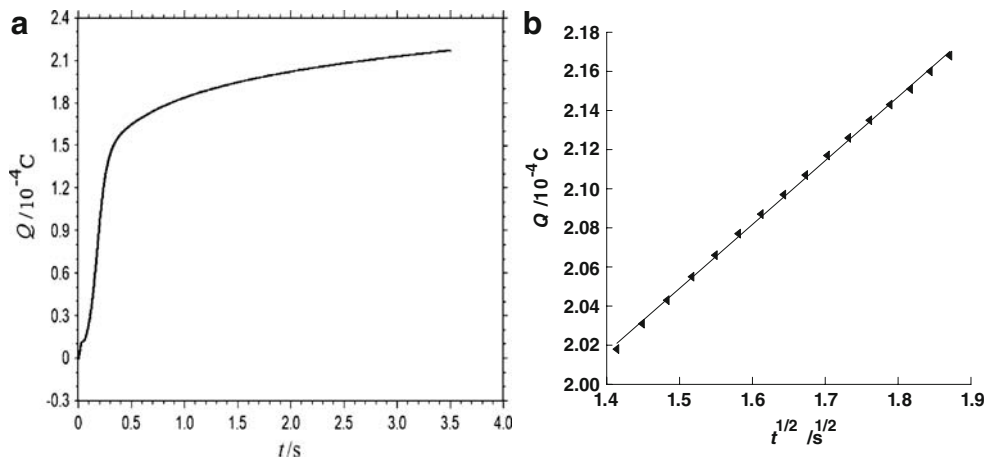
The chronocoulometric response of metal on the IL-CPE was investigated to calculate the diffusion coefficient ( $D$ ) of metal. Figure 4a showed the chronocoulometric curve of  $5.0 \times 10^{-4}$  mol/L metal and a good linear relationship between  $Q$  and  $t^{1/2}$  was shown in Fig. 4b. The linear regression equation was gotten as  $Q = 3.27 \times 10^{-5} t^{1/2} + 1.56 \times 10^{-4}$  ( $n=16$ ,  $\gamma=0.999$ ). According to Anson's equation [40]:  $Q = 2nFAD^{1/2}Ct^{1/2}/\pi^{1/2} + Q_{dl} + Q_{ads}$ , the diffusion coefficient ( $D$ ) of metal was calculated as  $6.35 \times$

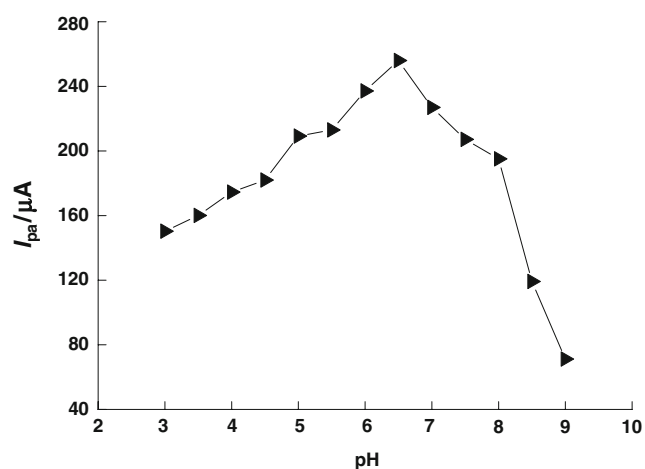
$10^{-5} \text{ cm}^2/\text{s}$ , which was about 3.5-fold larger than a previous reported value of  $1.823 \times 10^{-5} \text{ cm}^2/\text{s}$  [35]. The increase of the  $D$  value may be due to the higher conductivity of IL-CPE, which accelerated the electrode reaction of metal and then the increase of the diffusion coefficient.

#### Influence of buffer pH

The influence of buffer pH on the electrochemical response of metal was also investigated. The formal potential ( $E^0$ ) of metal shifted negatively as the solution pH increased in the range from 3.0 to 9.0, which indicated that protons were involved in the electrode

**Fig. 4 a** Chronocoulometric curve of  $5.0 \times 10^{-4}$  mol/L metal; **b** The relationship of  $Q$  vs.  $t^{1/2}$





**Fig. 5** Influence of buffer pH on the anodic peak current ( $I_{pa}$ ) for  $5.0 \times 10^{-4}$  mol/L metal

reaction. A good linear relationship was gotten between the formal potential ( $E^{0'}$ ) and the solution pH with the linear regression equation as  $E^{0'}$  (mV) =  $-62.2 \text{ pH} + 515.4$  ( $n=13$ ,  $\gamma=0.995$ ). According to the equation [41]  $-59.0x/n = -62.2$ , where  $x$  is the hydrogen ion participating the electrode reaction and  $n$  is the electron transfer number, the results indicated that the proton number involved is equal to the electron transfer number in the electrochemical reaction.

The influence of buffer pH on the anodic peak current was plotted and the results were shown in Fig. 5. It can be seen that the maximum value was gotten at pH 6.5. When the pH value exceeded 6.5, the peak currents began to decrease and even disappear with further increase of the

**Table 1** Influence of coexisting substances on the determination of  $1.0 \times 10^{-4}$  mol/L metal ( $n=6$ )

Coexisting substance	Concentration (mol/L)	Relative error (%)
2-Nitrophenol	$5.0 \times 10^{-5}$	-1.20
3-Nitrophenol	$5.0 \times 10^{-5}$	-2.34
Hydroquinone	$5.0 \times 10^{-5}$	2.09
Catechol	$5.0 \times 10^{-5}$	2.24
$K^+$	$2.0 \times 10^{-5}$	-0.68
$Cu^{2+}$	$2.0 \times 10^{-5}$	2.82
$Mg^{2+}$	$2.0 \times 10^{-5}$	4.15
$Zn^{2+}$	$2.0 \times 10^{-5}$	-1.52
$Ca^{2+}$	$2.0 \times 10^{-5}$	-0.37
$Mn^{2+}$	$2.0 \times 10^{-5}$	-2.55
$Pb^{2+}$	$2.0 \times 10^{-5}$	-2.14
$Al^{3+}$	$2.0 \times 10^{-5}$	-1.02
$Cl^-$	$2.0 \times 10^{-5}$	-0.94
$SO_4^{2-}$	$2.0 \times 10^{-5}$	-2.55

**Table 2** Determination results of metal in synthetic samples ( $n=5$ )

Sample no.	Added (mol/L)	Found (mol/L)	RSD (%)	Recovery (%)
1	$1.0 \times 10^{-5}$	$1.096 \times 10^{-4}$	1.65	96.00
2	$3.0 \times 10^{-5}$	$1.297 \times 10^{-4}$	2.08	99.00
3	$5.0 \times 10^{-5}$	$1.514 \times 10^{-4}$	1.80	102.80
4	$7.0 \times 10^{-5}$	$1.706 \times 10^{-4}$	3.51	100.86
5	$9.0 \times 10^{-5}$	$1.940 \times 10^{-4}$	2.74	104.44

The synthetic metal solutions were composed of  $1.0 \times 10^{-4}$  mol/L metal,  $7.5 \times 10^{-5}$  mol/L  $Zn^{2+}$ ,  $7.5 \times 10^{-5}$  mol/L  $Ca^{2+}$ ,  $7.5 \times 10^{-5}$  mol/L  $Cu^{2+}$ , and  $7.5 \times 10^{-5}$  mol/L  $Mg^{2+}$ .

buffer pH, so pH 6.5 B-R buffer was used for all the experiments.

#### Stability of IL-CPE

The stability of the IL-CPE was tested with  $5.0 \times 10^{-4}$  mol/L metal solution. After 30 continuous scans, 97.9% of the initial response was remained and after 70 continuous scans 96.7% of the initial response appeared. With the long time usage in the B-R buffer solution, the background current was also increased, which may be due partly to the dissociation of IL from the surface of IL-CPE. When not in use, the IL-CPE was stored in the  $4^\circ C$  refrigerator for about 3 weeks without a decrease of the response to metal, which showed good stability.

#### Analytical performance

Under the selected conditions, the determination of metal was performed on IL-CPE with cyclic voltammetry at the scan rate of 0.10 V/s. In the pH 6.5 B-R buffer, the anodic peak current was linear to the metal concentration over the range from  $5.0 \times 10^{-6}$  to  $1.0 \times 10^{-3}$  mol/L with the linear regression equation as  $I_{pa}$  ( $\mu A$ ) =  $-0.46C$  ( $\mu mol/L$ ) - 28.70 ( $n=11$ ,  $\gamma=0.994$ ) and the detection limit as  $2.33 \times 10^{-6}$  mol/L ( $3\sigma$ ). The relative standard deviation of 11 successive determinations of  $1.0 \times 10^{-5}$  mol/L metal gave the results of 3.27%, indicating that IL-CPE had good reproducibility.

**Table 3** Determination results of metal in photographic solutions ( $n=5$ )

Sample (mol/L)	Added (mol/L)	Found (mol/L)	RSD (%)	Recovery (%)
$1.0 \times 10^{-4}$	$1.0 \times 10^{-5}$	$1.102 \times 10^{-4}$	3.63	102.00
$1.0 \times 10^{-4}$	$3.0 \times 10^{-5}$	$1.307 \times 10^{-4}$	1.68	102.34
$1.0 \times 10^{-4}$	$5.0 \times 10^{-5}$	$1.494 \times 10^{-4}$	1.89	98.80
$1.0 \times 10^{-4}$	$7.0 \times 10^{-5}$	$1.694 \times 10^{-4}$	2.32	99.14
$1.0 \times 10^{-4}$	$9.0 \times 10^{-5}$	$1.876 \times 10^{-4}$	2.11	97.33

## Influence of coexisting substances

The influences of some coexisting substances such as metal ions, 2-nitrophenol, hydroquinone, etc. on the determination of  $1.0 \times 10^{-4}$  mol/L metol were investigated and the results were listed in Table 1. The results indicated that a few of them disturbed the determinations and the proposed method showed good selectivity.

## Sample determinations and recovery

The proposed method was further applied to detect the metol concentration in the synthetic samples and photographic solutions. Artificial wastewater samples containing metol, in which metal ions were added, were determined according to the general procedure. The analytical results were shown in Table 2. It can be seen that metol in the synthetic wastewater samples can be satisfactorily detected with the recovery in the range from 96.00% to 104.44%.

The photographic powder was purchased from Beijing Zhongjing Keyi Technology Limited Company and used for the preparation of the photographic solution, which was further determined by the proposed method with the calibration curve and the standard addition method. Table 3 presented the determination results, which indicated that the proposed method could be efficiently used for metol detection.

## Conclusions

The ionic liquid BPPF<sub>6</sub> modified carbon paste electrode was used to investigate the electrochemical behaviors of metol. The IL-CPE showed greatly improvement to the electrochemical response of metol and a pair of well-defined cyclic voltammetric peaks appeared, which was attributed to the specific characteristics of IL-CPE. Under the selected conditions, the anodic peak current was proportional to the metol concentration in the range from  $5.0 \times 10^{-6}$  to  $1.0 \times 10^{-3}$  mol/L with a detection limit of  $2.33 \times 10^{-6}$  mol/L ( $3\sigma$ ). There were no interferences from the commonly coexisting substances and the IL-CPE showed good selectivity and reproducibility.

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