

Selective Determination of Unsymmetrical Dimethylhydrazine on a Prussian Blue Modified Carbon Paste Electrode

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The electrocatalytic oxidation of unsymmetrical dimethylhydrazine (UDMH) has been studied on a Prussian Blue modified carbon paste electrode (PBMCPPE) by cyclic voltammetry technique. The results show that Prussian Blue acts as a suitable modifier for electron transfer in the oxidation of UDMH. A linear range of 3×10^{-5} to 1.15×10^{-3} mol L⁻¹, with a limit of detection (3σ) of 1.6×10^{-5} mol L⁻¹ was obtained using the amperometric method. The proposed sensor exhibited several advantages, including, namely, no interference from hydrazine, simple preparation, good stability and repeatability. Finally, the PBMCPPE was successfully applied for determination of UDMH in water samples.

Keywords: amperometric detection, Prussian Blue, unsymmetrical dimethylhydrazine, carbon paste electrode

Introduction

Unsymmetrical dimethylhydrazine (UDMH) is known as a relatively inexpensive fuel and, together with hydrazine, is a widely used rocket fuel.¹ UDMH is also used in the synthesis of polymers, pesticides, pharmaceuticals, and chemotherapeutic agents.² UDMH is a highly toxic volatile liquid and can be absorbed by oral, dermal, or inhalation routes of exposure, and is classified by the International Agency for Research on Cancer (IARC) as 2B carcinogens (possibly carcinogenic to humans).³ Different analytical methods have been reported for the determination of hydrazine and UDMH, such as acid-base and redox titration,⁴ optical,⁵ chemiluminescence,⁶ fluorimetry,⁷ gas chromatography,⁸ spectrophotometry flow injection,⁹ gas chromatography-mass spectrometry (GC-MS),^{1,4} and spectrophotometry.¹⁰ However, these methods suffer from various drawbacks, such as complexity, insufficient sensitivity or lack of portability of the instrumentation. Electroanalytical techniques seem to provide direct and efficient methods for the determination of hydrazine and UDMH, because of the opportunity for portable, cheap and rapid methodologies. Various electrochemical sensors have been applied to the determination of hydrazine and its derivatives.¹¹⁻¹⁵ However, to the best of our knowledge,

only one work reported on the electrochemical detection of UDMH.¹⁶ UDMH, as hydrazine, shows a large overpotential associated with the electrooxidation at conventional electrodes. It is a major challenge, which calls for the development of a high-performance catalyst for facilitating the oxidation process.

Ferric hexacyanoferrate, or Prussian Blue (PB), is one of the polynuclear transition-metal hexacyanometalates having an open, zeolite-like structure with well-known electrochromic,¹⁷ photo-physical,¹⁸ magnetic properties,¹⁹ and potential electroanalytical applications owing to their good catalytic properties.²⁰⁻²² Recently, PB modified electrodes have been used for the determination of various analytes, including glucose,²³⁻²⁵ hydrogen peroxide,²⁶⁻²⁸ hydrazine and its derivatives²⁹⁻³¹ and other compounds.^{32,33} In this work, an electrochemical sensor of Prussian Blue modified carbon paste electrode (PBMCPPE) was developed for UDMH determination in the presence of hydrazine.

Experimental

Chemicals and reagents

Unsymmetrical dimethylhydrazine (H₂NN(CH₃)₂) solution (99% purity) and hydrazine hydrate solution (H₂NNH₂·6H₂O, 50 wt.%) were purchased from Sigma-Aldrich. Paraffin oil, graphite powder (spectrum pure),

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potassium chloride (KCl), sodium hydroxide (NaOH), hydrochloric acid (HCl), dipotassium hydrogen phosphate (K_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), and potassium hexacyanoferrate ($K_3Fe(CN)_6$) were obtained from Fluka or Merck and used as received. The supporting electrolyte was 0.1 mol L^{-1} phosphate buffer solution (PBS) at pH 7 prepared with KH_2PO_4 and K_2HPO_4 . Deionized water was used to prepare all aqueous electrolyte solutions.

Apparatus

The electrochemical measurements were carried out with a μ Autolab (III) computer-controlled potentiostat and run with the General Purpose Electrochemical System (GPES) software. The electrochemical cell was assembled with a conventional three-electrode system consisting of Ag/AgCl/ 3 mol L^{-1} KCl (Metrohm, model 6.0733.100) as a reference electrode, a platinum wire (1 mm diameter) as a counter electrode and carbon paste electrode (2 mm diameter) as a working electrode. The pH was measured using a Metrohm 781 pH/mV meter. Scanning electron microscopy (SEM) images were obtained by using a scanning electron microscope (Philips, model XL30).

Synthesis of PB

The PB particles were synthesized according to the literature³⁴ with some modifications. A 50 mL aqueous solution of $K_3Fe(CN)_6$ (20 mmol L^{-1}) was added to a 25 mL aqueous solution of KCl (0.1 mol L^{-1}) and mixed with stirring. Then, 50 mL aqueous solution of $FeCl_3$ (20 mmol L^{-1}) was added. During 3 days, the blue precipitate of insoluble PB pigments was formed. The solution was centrifuged, washed with water three times and once with methanol and then dried at $80 \text{ }^\circ\text{C}$.

Preparation of chemically modified carbon paste electrode (CPE)

The prepared PB (0.01 g) was mixed for 35 min with graphite powder (0.45 g) and paraffin oil (0.3 mL) to produce a homogenous carbon paste. To fabricate PBMCPPE, the homogeneous paste was packed into a Teflon tube with a hole (3 mm diameter and 2 mm depth). The electrical contact was made by a copper wire connected to the paste in the inner hole of the tube. A fresh electrode surface was obtained by squeezing out a small portion of paste and polishing it with weighing paper. The modified carbon paste was kept at room temperature in a desiccator until used.

Results and Discussion

Characterization of PB particles

Figure 1 shows a SEM micrograph of the prepared PB particles. According to this Figure, Prussian Blue particles are cubic and have monodispersed sizes from less than 1 to $1.8 \mu\text{m}$. It is assumed that sharp edges because of the cubic nature of the particle provide better catalytic characteristics compared with spherical morphology.

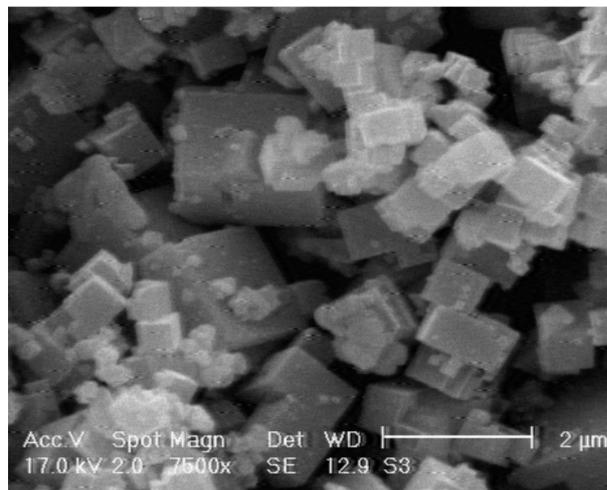


Figure 1. SEM image of PB particles.

Electrochemical behavior of modified electrode

The electrochemical behavior of the PBMCPPE was first investigated. Figure 2a shows cyclic voltammograms of the PBMCPPE at different scan rates (10 to 500 mV s^{-1}) in 0.1 mol L^{-1} phosphate buffer solution at pH 7. In the potential range of -0.3 to 0.55 V , a pair of reversible peaks is observed on the voltammograms. Peak separation ($\Delta E_p = E_{pa} - E_{pc}$) was at least 20 mV for the potential scan rate of 20 mV s^{-1} vs. Ag/AgCl. Also, the plots of anodic and cathodic peak currents against the sweep rates for both anodic and cathodic peaks are linear for sweep rates of 10 - 50 mV s^{-1} (Figure 2b). These results emphasize that the reduction of PB is an adsorption-controlled process. At sweep rates higher than 50 mV s^{-1} , the plot of i_p vs. $v^{1/2}$ (not shown) was linear, indicating a diffusion-controlled process, which might be related to the slow diffusion of potassium ions into the PB lattice. Similar results have been reported in the literature.^{26,35-39}

Electrochemical behavior of UDMH at a CPE and PBMCPPE

The cyclic voltammetric responses of a bare and modified carbon paste electrode in 0.1 mol L^{-1} PBS in

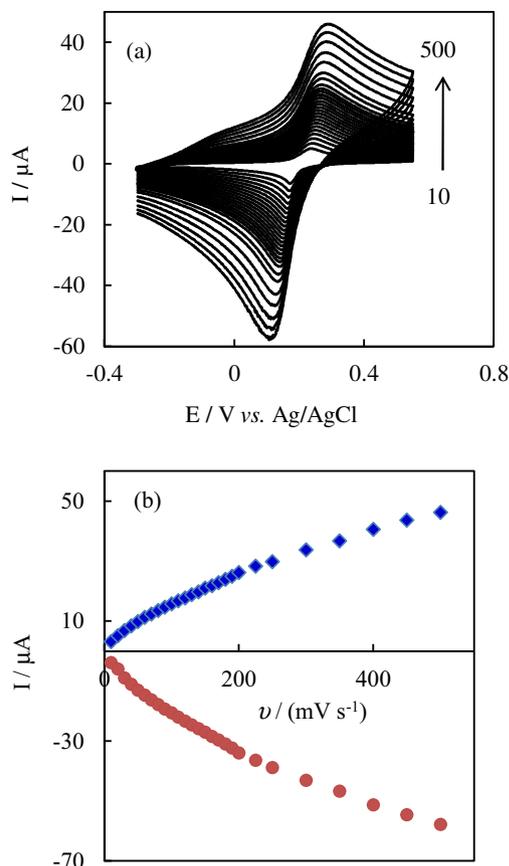


Figure 2. (a) Cyclic voltammogram response of a PBMCE in 0.1 mol L⁻¹ PBS (pH 7) at different scan rates: 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 225, 250, 300, 350, 400, 450 and 500 mV s⁻¹. (b) Plot of cathodic and anodic peak currents vs. scan rate.

the presence and absence of hydrazine and UDMH are shown in Figure 3. As it is seen from Figure 3A, scan c, at the bare carbon paste electrode, the oxidation of UDMH requires high positive potentials, leading to a poorly defined anodic wave involving very slow electrode kinetics. In contrast, oxidation of UDMH at the PBMCE (Figure 3B, scan f) in 0.1 mol L⁻¹ PBS (pH 7) occurred at much less positive potentials, associated with increasing anodic peak current while diminished in the cathodic peak current. The results indicated that the PB can act as a suitable modifier for electron transfer in the oxidation of UDMH at the carbon paste electrode. On the other hand, as can be seen in Figure 3B, scan e, the presence of hydrazine has no interference in the oxidation of UDMH. Therefore, an electrochemical technique can be developed for determination of UDMH in the presence of hydrazine.

Scan rate effect study

Figure 4a shows the cyclic voltammograms of a PBMCE at various scan rates obtained in 0.1 mol L⁻¹ PBS

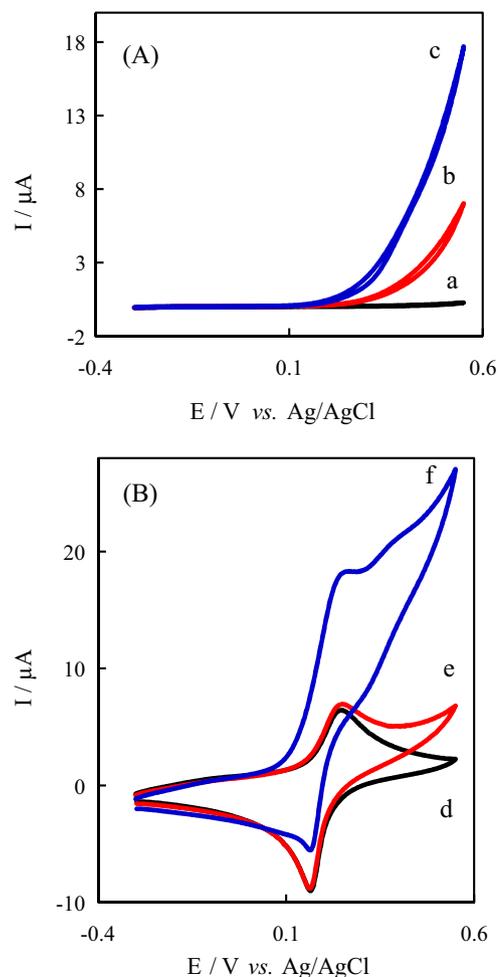


Figure 3. Cyclic voltammograms for CPE (A) and Prussian Blue modified carbon paste electrode (B). Scans (a) and (d) in 0.1 mol L⁻¹ PBS (pH 7); scans (b) and (e) in 0.1 mol L⁻¹ PBS (pH 7) containing 1 mmol L⁻¹ hydrazine; scans (c) and (f) in 0.1 mol L⁻¹ PBS (pH 7) containing 1 mmol L⁻¹ hydrazine plus 0.2 mmol L⁻¹ UDMH. Scan rates were 50 mV s⁻¹.

(pH 7) containing 0.1 mmol L⁻¹ UDMH. The nature of the oxidation process was found to be diffusion-controlled as evidenced from the linear plot of the peak current (I_p) vs. square root of the scan rate ($\nu^{1/2}$) for UDMH (Figure 4b). As Andrieux and Saveant⁴⁰ described, the transfer coefficient (α) for an overall irreversible electron transfer can be calculated from Figure 4c, according to the following equation:

$$E_p = b / 2 \log(\nu) + k \quad (1)$$

where b is the Tafel slope and the intercept of the plot of E_p vs. $\log(\nu)$ is constant. The slope of the linear regression is equal to $b / 2 = 0.059 / \alpha n$. Thus, b is $2(0.059 / \alpha n)$. The Tafel slope (b) was 109.4 mV decade⁻¹ (Figure 4c) and by considering that α equals 0.54, the results indeed suggest one-electron (n_α ca. 1) transfer process in the rate-determining step for the electrocatalytic oxidation

of UDMH. The transfer coefficient could be calculated by another method, i.e., it can be determined from the following equation at a scan rate of 200 mV s^{-1} :⁴¹

$$|E_p - E_{p/2}| = \frac{1.857RT}{\alpha F} = \frac{47.7}{\alpha} \text{ mV} \quad (2)$$

On the basis of equation 2, the transfer coefficient (α) was obtained as 0.52 which is in agreement with that obtained from equation 1.

Study of pH-dependence

In general, pH is one of the variables, which commonly and strongly influences the current, and shape of voltammograms. In order to choose the best pH solution for UDMH detection, the effect of pH was investigated on the response of PBMCPPE in a large range of pH from 2.5 to 10 using PBS. The pH was adjusted by adding small amounts

of hydrochloric acid or potassium hydroxide, maintaining the volume of the electrolyte approximately constant. Figure 5 shows the relationship between peak current and pH value for the PBMCPPE in the presence and absence of UDMH. As can be observed, the I_p of PBMCPPE decreases in alkaline solution, while the response increases with the pH up to a maximum of 7. This behavior could be explained as follows: UDMH has basic nature and is unstable in acidic environment. On the other hand, in alkaline solution ($\text{pH} > 8$) PB is decomposed by hydroxide ions.³⁷ Thus, the utility of this modified electrode is eventually limited to neutral solutions.

Analytical performance characteristics

Amperometric measurements were carried out at 250 mV by injection of UDMH solution (20 mmol L^{-1}) to a continuously stirred (800 rpm) phosphate buffer solution ($\text{pH} 7$). Figure 6a shows a typical current-time response

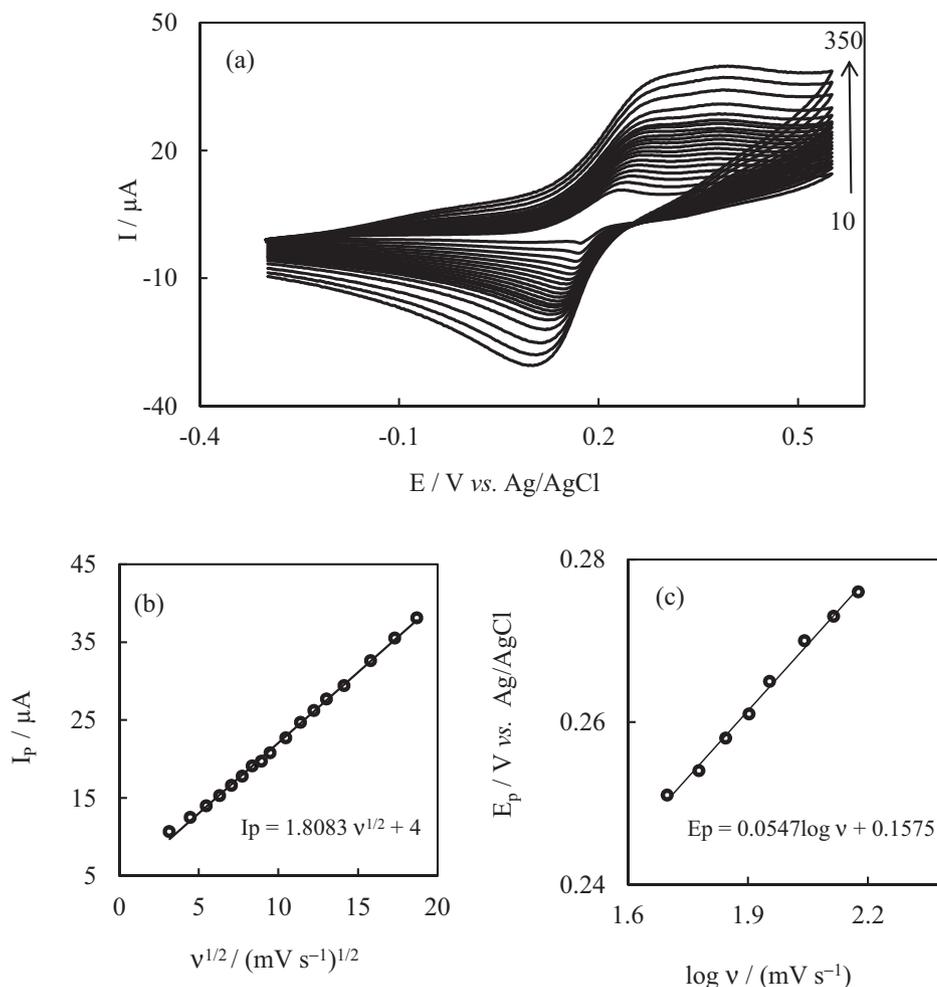


Figure 4. (a) Cyclic voltammograms of PBMCPME in 0.1 mol L^{-1} PBS ($\text{pH} 7$) containing 0.1 mmol L^{-1} UDMH at scan rates 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 170, 200, 250, 300 and 350 mV s^{-1} . (b) The plot of anodic peak currents against the (sweep rates)^{1/2} for anodic peaks for sweep rates of $10\text{-}350 \text{ mV s}^{-1}$. (c) Tafel plot.

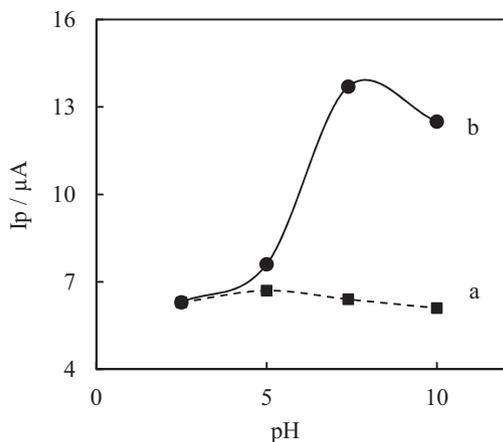


Figure 5. Response of the Prussian Blue modified carbon past electrode in the absence (scan a) and presence of 0.1 mmol L^{-1} UDMH (scan b) in the pH range of 2.5-10.

of the PBMCPe on successive step changes of UDMH concentration. It can be seen that the amperometric signal is stable after the injection of UDMH and the electrode response time is very short (less than 3 s). Figure 6b displays the corresponding calibration curve for UDMH. Under the present condition, the steady-state current has a

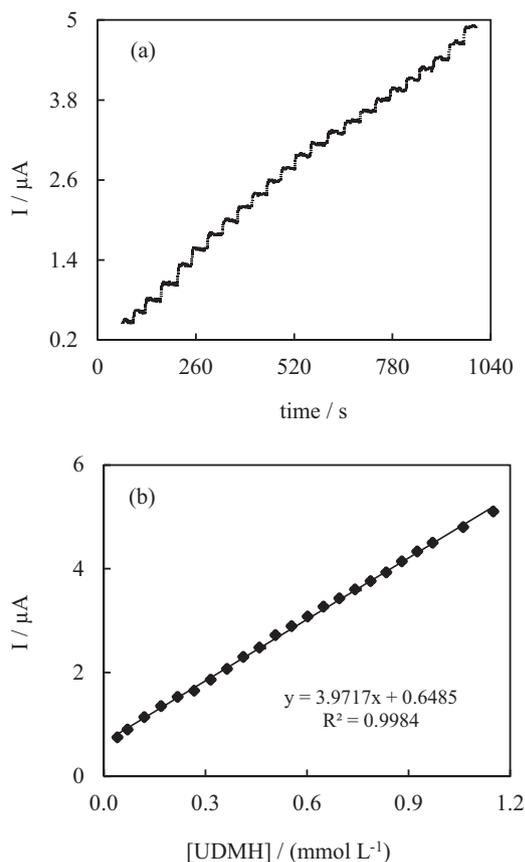


Figure 6. Amperometric response of Prussian Blue modified carbon past electrode to successive injections of UDMH (a); calibration curve of UDMH concentration at the modified electrode (b). Other conditions: 0.1 mol L^{-1} PBS (pH 7) at 250 mV.

linear relationship with the concentration of UDMH in the range from 3×10^{-5} to $1.2 \times 10^{-3} \text{ mol L}^{-1}$ with a detection limit of $1.6 \times 10^{-5} \text{ mmol L}^{-1}$ ($S/N = 3$), sensitivity of $3.97 \mu\text{A L mmol}^{-1}$ and correlation coefficient (R^2) = 0.9984.

The day-to-day stability of the PBMCPe was evaluated by measuring the anodic peak current response at a fixed $5.0 \times 10^{-4} \text{ mol L}^{-1}$ concentration over a period of five months. At the end of five months the response current decreased by a factor less than 5% and relative standard deviation (RSD) of 4% for 15 measurements. This shows good stability and reproducibility of the PBMCPe and can be used in routine analysis.

Interference study

To apply this method to determine UDMH in environmental water samples, the influence of common substances as potential interference compounds (0.05 mol L^{-1}) on the determination of UDMH was studied under the optimum conditions with UDMH concentration of 0.05 mmol L^{-1} . The tolerance limit was defined as the maximum concentration of the potential interfering substance causing an error less than 3% for the determination of 0.05 mmol L^{-1} of UDMH. Various interferent-to-analyte ratios (tolerance limit molar ratio) causing less than $\pm 3\%$ relative error for a UDMH concentration of 0.05 mmol L^{-1} is listed in Table 1, which indicates that most cations and anions do not interfere with this amperometric method for UDMH determination.

Table 1. Effect of some foreign ions on the determination of 0.05 mmol L^{-1} UDMH under optimized conditions

Foreign species (0.05 mol L^{-1})	Maximum tolerable concentration ratio
Na^+ , K^+ , NH_4^+ , Ca^{2+} , Mg^{2+} , Ba^{2+} , Co^{2+} , Mn^{2+} , Zn^{2+} , Ni^{2+} , Cu^{2+} , Cr^{3+}	1000
F^- , Cl^- , Br^- , NO_3^- , CH_3COO^- , H_2PO_4^- , HPO_4^{2-} , SO_4^{2-} , CO_3^{2-} , PO_4^{3-}	1000
Urea, nitrourea, thiourea, hexamine	1000

Determination of UDMH in water samples

To demonstrate the applicability of the proposed method for the analysis of a real sample, three water samples from different sources consisting of drinking water, river water and well water were spiked with UDMH and were analyzed under optimized conditions using the above technique. UDMH content of all samples was determined by PBMCPe using standard addition method. The obtained results are summarized in Table 2. As it is obvious, the recovery of UDMH was found to be between 98.6 and 104.0% and RSD

Table 2. Results of determination of UDMH in water samples

Water sample	UDMH content		Recovery / %	RSD / % (n = 5)
	Added / (10^{-6} mol L $^{-1}$)	Found / (10^{-6} mol L $^{-1}$)		
River water	176	183	104.0	2.3
	254	255	100.4	1.1
	349	344	98.6	1.6
Drinking water	176	174	98.9	3.7
	254	261	102.8	2.7
	349	348	99.7	1.2
Well water	176	181	102.8	3.6
	254	262	103.2	1.6
	349	355	101.7	1.2

was between 1.1 and 3.7% using the amperometric method. This means that the proposed procedure should be applicable to the analysis of real samples with different matrices.

Conclusions

A carbon paste electrode modified with PB has been fabricated and used for determination of UDMH in the presence of hydrazine. The results demonstrated that the electrooxidation of UDMH at the surface of PBMCPPE occurs at a potential of about 220 mV and less positive than bare carbon paste electrode. The modified electrode is simple, sensitive, rapid, and economical for the determination of UDMH. The voltammetric result indicates that the PBMCPPE prepared with the present method shows a stable electrochemical behavior. The oxidation process was pH-dependent and a higher catalytic current was observed about pH 7. The electrocatalytic response shows a linear relationship on the concentration of UDMH in the range of 30 to 1150 $\mu\text{mol L}^{-1}$, with a limit of detection of about 16 $\mu\text{mol L}^{-1}$. Finally, this method was used for the determination of UDMH in water samples using the standard addition method. The PB modified CPE with its low cost and ease of preparation seems to be of great utility for further sensor development.

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