

DETERMINATION OF TRACE NITRITE BY DIFFERENTIAL PULSE VOLTAMMETRY USING MAGNETIC MICROSPHERESMing YANG¹ and Hu Lin LI^{2,*}*Department of Chemistry, Lanzhou University, Lanzhou 730000, China;**e-mail: ¹ yangmlzu@yahoo.com.cn, ² lihl@lzu.edu.cn*

Received January 28, 2002

Accepted June 17, 2002

A new type of magnetic polymer microspheres containing methylamino groups on the surface was synthesized. It can be reacted with nitrite to produce electroactive *N*-nitroso compound. On reduction of this derivative collected on the magnetic electrode, nitrite can be determined. Under optimum conditions, the peak potential (E_p) of the derivative is -0.72 V (vs Ag/AgCl). Nitrite in the range 1 – 800 $\mu\text{g l}^{-1}$ can be determined, the detection limit being 0.5 $\mu\text{g l}^{-1}$. The relative standard deviation for determination of 100 $\mu\text{g l}^{-1}$ nitrite was 1.96% . The method was used in the determination of nitrite in water samples with satisfactory results.

Keywords: Nitrites; Voltammetry; Magnetic microspheres; Methylamino groups; Nitroso compounds; Electroreduction.

The toxicity of nitrite is primarily due to its interaction with blood pigment to produce methemoglobinemia. The important role of nitrite in producing *N*-nitrosamines, some of which have been shown to be human carcinogens, is well established¹. The occurrence of nitrite salts in the environment and their use as food preservatives is widespread. The level of organic pollution in water is indicated by nitrite². Thus a sensitive method for the determination of nitrite is desirable. In recent years, many methods have been proposed for the determination of nitrite. These include spectrophotometry³, liquid chromatography⁴, fluorophotometry^{5,6} and voltammetry⁷. Composite magnetic polymer microspheres usually contain two parts: one is the magnetic core which is always an inorganic magnetic material, such as Fe_3O_4 , $\delta\text{-Fe}_2\text{O}_3$; the other part is the polymer shell around the magnetic core. The microspheres can moved in magnetic field and be separated from the medium. The polymer shell, always containing some active groups, can covalently bond organic molecules, biomolecules and cells. Magnetic microspheres have been used in fluoroimmunoassay⁸, flow injection analy-

sis^{9,10}, chemiluminescence enzyme immunoassay¹¹, mRNA recovery¹², DNA carriers¹³ and environmental analysis¹⁴.

In this paper, an indirect voltammetric determination of nitrite is reported. The microspheres containing methylamino groups on the surface can react with nitrite to produce *N*-nitroso compounds which are concentrate on a magnetic electrode. The current of the reduction peak was measured at -0.72 V (vs Ag/AgCl) by differential pulse voltammetry (DPV). This determination is a highly sensitive and selective procedure.

EXPERIMENTAL

Reagents

All chemicals were of the highest purity. Triply distilled water was used throughout. A nitrite stock standard solution (1.00 g l⁻¹) was prepared by dissolving 1.500 g of sodium nitrite in distilled water and diluting to $1\ 000$ ml. Nitrite working standard solutions were prepared daily from the stock standard solution by appropriate dilution with water.

Apparatus

All electrochemical experiments were carried out using an electrochemical analyzer BAS100w (U.S.A.). The working electrode used in DPV was a silver-based mercury-film magnetic electrode with an area of 0.10 cm². The structure of the silver-based magnetic electrode is shown in Fig. 1, it was obtained from the magnetic material factory of Lanzhou. The mercury-film was electroplated¹⁵ on the polished electrode surface for 2 min with constant current 6 mA in saturated Hg(NO₃)₂ solution and then the electrode washed with distilled water. The inner sleeve was made of diamagnetic copper. A large-area platinum plate was

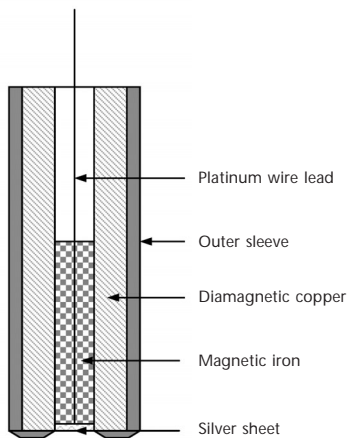


FIG. 1
Structure of the silver-based magnetic electrode

used as the counter electrode. All potential measured and reported in this paper were vs Ag/AgCl (saturated KCl) electrode.

Preparation of Magnetic Microspheres

A series of microspheres was synthesized by dispersion copolymerization. Fe_3O_4 powder (Lanzhou Institute of Magnetic Materials) with a particle size in the 10–80 nm range was dispersed ultrasonically in poly(ethylene glycol)–water solution. The mixture was placed in a 250-ml round-bottomed, four-necked flask with a H_2O –EtOH incubating dispersion medium. Styrene and pent-4-ene-2-one were copolymerized using potassium persulfate as the initiator. The reaction mixture was stirred at 400 rpm for 6 h, while the reaction temperature was kept at 70 °C and N_2 gas was passed continuously through the flask. The polymer was washed with distilled water, ethanol and heated with a solution of 0.5 g *N*-methyl-1,4-phenylenediamine in 80 ml of ethanol at 80 °C for 4 h while stirring. The magnetic microspheres were separated in a magnetic field and washed with 20% ethanol until the filtrate was colorless. A suspension of magnetic microspheres (1 g l^{-1}) containing CH_3NH groups on their surface was prepared by appropriate dilution with ethanol and water. A TEM photograph of magnetic microspheres is shown in Fig. 2.

Procedure

The supporting electrolyte was 0.1 mol l^{-1} AcOH (pH 2.9). A 25-ml volumetric flask containing a suitable amount of nitrite, buffer solution and 5.00 ml of a magnetic microspheres solution was heated in a water bath for 25 min and then diluted to the mark. This solution was placed in a H-shape cell, then a stream of nitrogen was passed through for 5 min in order to remove oxygen. An initial potential of -0.50 V (vs Ag/AgCl), a final potential of -0.90 V , a scan rate of 6 mV s^{-1} , a pulse amplitude of 80 mV, a sample width of 15 ms, a pulse width of 50 ms, a pulse period of 1 200 ms, a past time of 30 s were found to be the optimum conditions. The current of the reduction peak (as shown in Fig. 3) was measured at -0.72 V (vs Ag/AgCl) using DPV on a silver-based mercury-film magnetic electrode. The results were obtained by plotting the related peak current against the concentration of freshly prepared standard solutions.

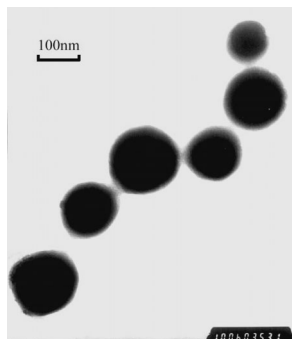


FIG. 2
TEM of magnetic microspheres

RESULTS AND DISCUSSION

Supporting Electrolyte and pH

DPV curves was observed in the following electrolytes: $\text{H}_3\text{PO}_4\text{-KH}_2\text{PO}_4$, HCl-KCl and AcOH , but high sensitivity and stability could be achieved only in AcOH . The magnetic microspheres have a poor stability as pH lower than 2.0; hence pH 2.0–4.0 were studied. As shown in Table I, the peak height increased with the increasing pH of the medium at pH 2.0–2.6, then it was confirmed stable at pH 2.6–3.2, and decreased on increasing pH from 3.2 to 4.0. On the basis of these results, a supporting electrolyte of 0.1 mol l^{-1} AcOH (pH 2.9) was chosen.

TABLE I
Effect of pH on peak current for $10.0 \mu\text{g l}^{-1}$ nitrite

pH	2.0	2.4	2.6	2.8	3.0	3.2	3.4	3.6	4.0
Peak current, nA	232	240	247	248	248	246	223	199	157

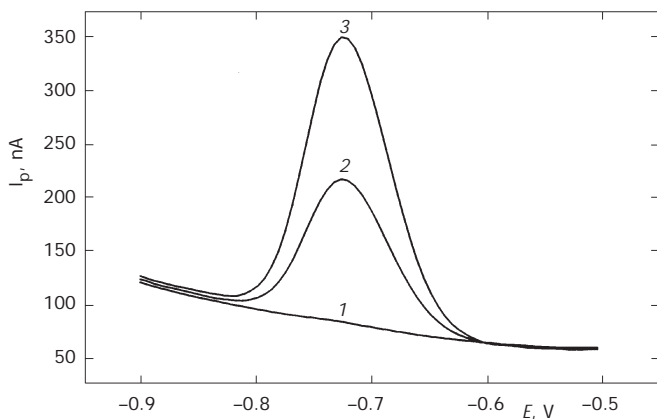


FIG. 3
Differential pulse voltammograms of mixtures 0.1 mol l^{-1} AcOH - 0.20 g l^{-1} magnetic microspheres with nitrite: 1 0.00 , 2 5.00 , 3 $10.00 \mu\text{g l}^{-1}$

Working Electrode and Effect of Heating Time

A glassy carbon electrode, silver electrode, platinum electrode and silver-based mercury-film magnetic electrode were tried as working electrodes. Only silver-based mercury-film magnetic electrode showed a peak current of nitrite. The nitrite reacted with magnetic microspheres slowly at room temperature. The peak heights were used to adjust the extent of the reaction between nitrite and magnetic microspheres. It was found that the peak current of the formed derivative increased with the heating time up to 25 min and then reaching a maximum, constant value (Fig. 4).

Influence of the Scan Rate on the Peak Current

The change of the peak current with the scan rate was also investigated. With increasing sweep rate ($v < 10 \text{ mV s}^{-1}$), the peak current was found to increase. Larger peak currents can be obtained at higher scan rates, but then the reduction peak broaden. On the basis of these findings, a scan rate of 6 mV s^{-1} was chosen for all further measurements.

Interferences

In order to investigate the selectivity of the reaction, several cations, anions and organic compounds were tested with a standard solution of nitrite

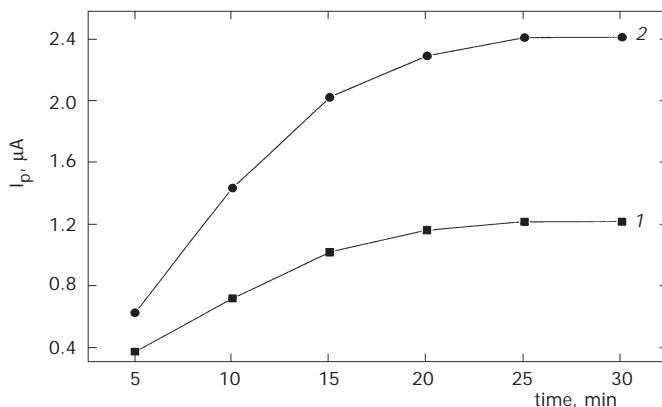


FIG. 4
Effect of heating time on peak current for mixtures $0.1 \text{ mol l}^{-1} \text{ AcOH}$ - 0.20 g l^{-1} magnetic microspheres with nitrite: 1 50 , 2 $100 \mu\text{g l}^{-1}$

(50 $\mu\text{g l}^{-1}$). No interference K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Mn^{2+} , Fe^{3+} , Zn^{2+} , Cu^{2+} , Cd^{2+} , Pb^{2+} , NH_4^+ , Cl^- , F^- , NO_3^- , SO_4^{2-} and PO_4^{3-} at concentrations up to 0.5 g l^{-1} was observed. Similarly was observed with methanol and ethanol at concentrations 50 g l^{-1} , with benzene and acetone at concentrations up to 1 g l^{-1} . Aniline interfered only at concentrations higher than 10 mg l^{-1} .

Application

The proposed method was used for the determination of nitrite in samples of industrial waste water and river water. The results were compared with a standard method¹⁶ for the determination of nitrite. Determination of nitrite and recovery of nitrite in water samples are given in Table II.

TABLE II
Determination of nitrite and nitrite recovery in water samples ($n = 5$)

Water	Nitrite found, $\mu\text{g l}^{-1}$		Added $\mu\text{g l}^{-1}$	Found $\mu\text{g l}^{-1}$	Recovery %	RSD %
	Proposed method	Standard method ref. ¹⁶				
Industrial waste	258	260	300	556	99.3	1.71
River	69	70	70	138	98.6	2.26

Calibration, Precision and Detection Limit

The DPV peak was found to increase linearly with the concentration in the range of 1–800 $\mu\text{g l}^{-1}$ of nitrite. The linear regression equation is I_p (nA) = $5.3 + 24.3C$ ($\mu\text{g l}^{-1}$) (correlation coefficient 0.996). Five successive determinations at nitrite concentrations 10, 100 and 500 $\mu\text{g l}^{-1}$, gave relative standard deviations (RSD) 3.17, 1.96 and 1.63%, respectively. The detection limit was 0.5 $\mu\text{g l}^{-1}$.

Comparative Measurement

Comparative measurements were carried out under the optimum conditions. The results of tests are shown in Table III. There was no peak current

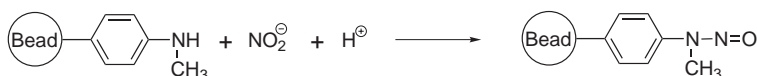
for nitrite ($100 \mu\text{g l}^{-1}$) without the reagent. Using *N*-methylaniline as the reagent, the peak current was small. Hence, the magnetic microspheres have a clear effect on sensitivity of the voltammetric determination.

TABLE III
Peak current in comparative measurements

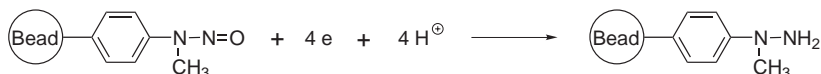
Reagent	Peak current, μA	
	$10 \mu\text{g l}^{-1} \text{NO}_2^-$	$100 \mu\text{g l}^{-1} \text{NO}_2^-$
Magnetic microspheres	0.248	2.421
<i>N</i> -Methylaniline	0.000	0.016
None	0.000	0.000

Reaction Path

From the above mentioned effects of pH, reaction time, scan rate, it is reasonable to propose the following reaction path. The magnetic microspheres react with nitrite to produce *N*-nitroso compounds as confirmed by IR data ($\nu_{\text{NO}} 1460 \text{ cm}^{-1}$):



The nitroso group can be reduced at a silver-based mercury film magnetic electrode:



CONCLUSION

The procedure described was shown to be one of the most sensitive voltammetric methods for nitrite determination. The interference of common ions and compounds is low. The procedure can be used as a selective method for the determination of nitrites in aqueous medium.

This work was supported by the National Nature Science Foundation of China.

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