Flow Injection Amperometric Detection of Sulfide Using a Prussian Blue Modified Glassy Carbon Electrode

Bensu ERTEK,* Dai Long VU,** Libor ČERVENKA,** and Yusuf DILGIN*†

*Canakkale Onsekiz Mart University, Science & Art Faculty, Department of Chemistry, 17100 Canakkale, Turkey

**Department of Analytical Chemistry, Faculty of Chemical Technology, University of Pardubice, Studentská 573, Pardubice 532 10, Czech Republic

This study investigates a new approach for the electrocatalytic determination of sulfide in a flow injection analysis (FIA) system using a Prussian blue modified glassy carbon electrode (PB/GCE). The results from experiments show that PB/GCE significantly enhances the electrocatalytic activity towards sulfide oxidation. A homemade flow electrochemical cell was used to perform the electrocatalytic determination of sulfide in the FIA system. The currents obtained from amperometric measurements in the FIA system at optimum conditions (carrier solution, pH 8.0; Britton–Robinson buffer solution containing 0.1 M KCl; flow rate, 1.4 mL/min; transmission tubing length, 10 cm; injection volume, 100 μ L; constant applied potential, +150 mV vs. Ag/AgCl/KCl(sat)) were linearly correlated with the sulfide concentration. A calibration curve was obtained for sulfide concentrations in the range of 0.5 – 100 μ M. The detection limit was found to be 0.3 μ M for the amperometric method. The proposed method was successfully applied to wastewater sample. Finally, results from sulfide measurements by PB/GCE were in good agreement with those obtained from the spectrophotometric method.

(Received June 30, 2012; Accepted September 5, 2012; Published November 10, 2012)

Introduction

Sulfide is a common type of organosulfur compound that is well known for its bad odors and toxicity. Even at a low concentration, sulfide can lead to personal distress, whilst at a higher concentration it can result in the loss of consciousness, permanent brain damage or even death.¹ In aquatic environments, it can be released through the anaerobic degradation of organic materials and the reduction of sulfate due to bacterial anaerobic respiration.² Besides, sulfide salts are frequently used in industrial waste streams to minimize the transport of several toxic metals, such as mercury, and get into the environment through precipitation reactions. Sulfide concentrations in water and wastewater solutions are analytically determined as total sulfide, or as reactive sulfide concentrations. The determination of total sulfide and sulfide species has been of a significant interest for analytical and environmental chemists.

Several techniques have been developed to determine sulfide in natural water as well as in wastewater. However, the major difficulty in the analysis of this target is a lack of stable sulfide standards. The iodometric titration method can offer a simple procedure without sulfide standard, but it is not sensitive enough for samples with low concentration of sulfide due to its low detection limit (1 mg/L).³ A spectrophotometric method, which is based on the reaction of aqueous sulfide with *N,N*-dimethyl-phenyl-1,4-diamine to produce methylene blue, has been used widely due to its higher sensitivity compared with the traditional

titrimetric method.⁴ High-performance liquid chromatography and gas chromatography have also been used for the indirectly determination of sulfide.^{5,6} However, these methods require specific equipment which is very expensive and difficult in monitoring. Electrochemical techniques, however, have some advantages, such as easy application, lower cost and providing direct, sensitive and fast detection of lower concentrations of H₂S.^{7–24}

The direct electrochemical oxidation of sulfide is highly irreversible with a great overpotential at bare electrodes. Additionally, the oxidized products of sulfide can be adsorbed on the electrode surface, which may result in fouling and passivation of the electrode surface, leading to poor sensitivity, poor selectivity and unstable analytical signals. In order to overcome these problems, modifications of the electrode surface with redox mediators have been extensively used. Amperometric redox mediators based sensors, which used ferricyanide,^{7–9} ferrocene carboxylate,¹⁰ ferrocenesulfonate,^{11,12} *N,N*-diphenyl-*p*-phenylenediamine,¹³ cobalt pentacyanonitrosylferrate,¹⁴ vanadium pentoxide,¹⁵ cinder/tetracyano nikelate,¹⁶ hexadecylpyridinium-bis(chloranilato)-antimonyl(V),¹⁷ 2,6-dichlorophenolindophenol¹⁸ and 2-(4-fluorophenyl)indolemodified xerogel,¹⁹ have been applied recently. Recently, our research has considered electrocatalytic effects of some redox mediators towards sulfide oxidation; such as methylene blue (MB),²² quercetin²³ and hematoxylin²⁴ showed significant enhancement of sensitive and reliable response of sulfide.

Among the various redox mediators, Prussian blue (PB) (iron(III) hexacyanoferrate) is widely applied in numerous fields, such as electrochromism,²⁵ ion selective electrodes,²⁶ protection against corrosion,²⁷ solid-state batteries²⁸ and

† To whom correspondence should be addressed.
E-mail: ydilgin@yahoo.com

electrocatalysis.²⁹ A recent review by Karyakin³⁰ demonstrates its potential applications in the field of electroanalysis.

In the present work, a PB/glassy carbon electrode (GCE) was used to study the catalytic effect of PB towards sulfide oxidation in the flow injection analysis (FIA) system.

Experimental

Reagents and equipments

All chemicals, including sodium sulfide, FeCl_3 and $\text{K}_3\text{Fe}(\text{CN})_6$, used in this study were of analytical reagent-grade (Merck) and used without further purification. The solutions used throughout this work were always prepared using deionized water from a Milli-Q (Millipore, Bedford, USA) device. The stock solution of Na_2S (0.1 M) was prepared by dissolving $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ crystals in a degassed solution (0.1 M NaOH), and kept at $+4^\circ\text{C}$ for maximum one week. This solution was periodically standardized by an iodometric method. Britton-Robinson (BR) buffer solution with pH 8.0 containing 0.1 M KCl was used as a supporting electrolyte for amperometric studies on the electrocatalytic oxidation of sulfide determination in the FIA system. Cyclic voltammetric and amperometric experiments were performed in a traditional three-electrode system. A platinum wire, an Ag/AgCl/KCl(sat) and a PTFE-shrouded GCE (MF2012 Bioanalytical System, 3 mm diameter) were used as the counter electrode, reference electrode and working electrode, respectively.

All electrochemical experiments were carried out using a Compactstat Electrochemical Interface (Ivium Technologies, Eindhoven, Netherlands). The pH values of the solutions were measured using an HI 221 Hanna pH-meter with a combined glass electrode (Hanna HI 1332). A homemade electrochemical flow cell constructed from Teflon was used for the electrocatalytic detection of sulfide in FIA.³¹ An eight-channel Ismatec, Ecoline peristaltic pump with polyethylene tubing (0.75 mm i.d.) and a Rheodyne 8125 sample injection valve were used to conduct the FIA experiments. The sulfide concentration was measured based on the MB reaction using a UV-Vis spectrometer (Perkin Elmer Lambda 35). The GCEs were cleaned in an ultrasonic bath (Bandelin Sonorex RK 100H) prior to their modification.

Electrochemical procedure

Before a modification, GCE was polished with alumina (Al_2O_3 , grain size 1 μm , 0.3 μm , 0.05 μm , respectively) on a polishing cloth, and then GCE was sonicated in ethanol and deionized water. The composite films were prepared in two steps. The first step was the composition of PB on GCE in a solution containing 1.25 mM FeCl_3 , 1.25 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 0.1 M KCl, 0.1 M HCl by applying a working potential of 0.4 V for 40 s. After washing with pure water, the electrode was left to dry at 100°C for 1 h. Then, the modified electrode was immersed in a phosphate buffer solution of pH 6.0 (0.05 M $\text{Na}_2\text{HPO}_4/\text{NaH}_2\text{PO}_4$ and 0.1 M KCl) for electrochemical activation by applying a potential of -0.05 V vs. Ag/AgCl for 600 s. After that, nafion membrane was prepared by syringing an amount of 3.0 μL on the electrode. The solvent in nafion was allowed to evaporate under ambient temperature.

Flow injection analysis procedure

The PB/GCE or bare GCE, Pt wire and Ag/AgCl electrode were inserted into a homemade electrochemical flow cell. In order to obtain stable results in the FIA system, PB/GCE was prepared according to the procedure mentioned above in the presence of 14 mM pyrrole. This polypyrrole-doped PB/GCE

was used in the FIA system. After a steady background current was obtained under the optimum conditions (a sample loop of 100 μL , a flow rate of 1.4 mL/min, an applied potential of +150 mV vs. Ag/AgCl/KCl(sat), a length of tubing of 10 cm and carrier stream of pH 8.0 BR buffer containing 0.1 M KCl), various concentrations of sulfide were injected into the system, and then the current-time curve was recorded. In all FIA experiments, at least three injections were made for each sulfide standard solution.

Sample preparation

PB/GCE was also tested using wastewater samples. For this purpose, the samples were collected from the Kepez municipal wastewater treatment plant in Canakkale, Turkey. All samples were filtered to remove particulate matter. Because organic and inorganic ingredients of the wastewater samples may interfere with the analysis, the sulfide was transferred in H_2S form using a separation system, similar to that proposed by Mousavi and Sarlack.³² The separating system used in this study includes four flasks and a separating funnel. A 50-mL portion of wastewater sample was placed in the first flask. A 10-mL portion of base solution (0.1 M NaOH + 0.1 M KCl) was placed in the second flask, a 10-mL portion of BR buffer solution pH 8.0 including 0.1 M KCl was placed in the third flask and finally a 30-mL portion of base solution (0.1 M NaOH + 0.1 M KCl) was placed in the fourth flask. All of those flasks were sequentially connected with a rubber column. A 10-mL portion of concentrated HCl was added to the first flask from the separating funnel and heated for about 15 min at boiling points; then, argon gas was passed through this system. In this way all sulfide species were absorbed in the second, third and fourth flasks in the form of H_2S . The solutions in the flasks were mixed, and the pH of the final solution was arranged to 8.0 with 0.1 M HCl or 0.1 M NaOH; then, the sulfide content was determined by the amperometric FIA system using PB/GCE. Samples obtained from 16.06.2012 were diluted about ten times before injection of the solution to system.

Results and Discussions

Electrochemical behavior of PB/GCE

Figure 1 showed a cyclic voltammogram in a BR buffer solution (pH 8.0) containing 0.1 M KCl. As can be seen from the figure, an anodic peak and cathodic peak were observed at +100 and +50 mV, respectively. The formal potential of the redox process was +75 mV and the separation between the peak potentials was +50 mV. The reverse-to-forward peak current ratio was approximately unity, which reflects the reversible electrochemical behavior of PB. Besides, the peak currents decreased after the first few cycles, and then tended to be stable.

The electrochemical behavior of PB/GCE was investigated by recording cyclic voltammograms in a BR buffer (pH 8.0) containing 0.1 M KCl at various scan rates. The anodic (I_{pa}) and cathodic (I_{pc}) peak currents were found to be linear proportional to the scan rate in the range of 10 and 800 mV/s. The equations and regression coefficients for anodic and cathodic peaks were found to be: $I_{\text{pa}} = 4.11v^{1/2} - 16.90$ ($R^2 = 0.9866$) and $I_{\text{pc}} = -3.36v^{1/2} - 14.09$ ($R^2 = 0.9843$), respectively (where $v^{1/2}$ is the square root of scan rate). These results indicate that mass-transport process occurred mainly by diffusion.

In order to study the effect of the pH on the electrochemical behavior of PB/GCE, BR buffers with a wide range of pH from 2 to 10 were used as supporting electrolytes in recording cyclic voltammograms of PB/GCE at a scan rate of 50 mV/s. It was

observed that the pH significantly influenced the electrochemical behavior of PB/GCE, since the current peaks obtained in acidic medium (pH 2.0, 3.0, 4.0) were slightly higher and sharper than those obtained at pH values between 5.0 and 10.0. This phenomenon was caused by the stability of the modified electrode in different pH medium. In basic solutions, ferric ion can strongly interact with hydroxide to form ferric hydroxide. In the literature, it is reported that at pH higher than 6.4, ferric hydroxide is formed, while Fe-CN-Fe bonds are destroyed and PB is dissolved from the electrode surface.³⁰

Besides, the surface morphology of the modified electrode was also investigated by capturing their scanning electron microscope SEM images. As shown in Fig. 2, a bare electrode obtained a smooth surface, while a modified electrode gave a rough surface caused by PB coating.

Electrocatalytic activity of PB/GCE towards sulfide oxidation

Cyclic voltammograms of PB/GCE were recorded in both the presence and absence of sulfide to investigate the electrocatalytic activity of PB/GCE towards sulfide oxidation. Figure 3 shows cyclic voltammograms of PB/GCE in a BR buffer solution (pH 8.0) containing 0.1 M KCl at 50 mV/s in the absence of sulfide. Anodic and cathodic peaks were observed at +100 and

+50 mV, respectively. The electrochemical oxidation of sulfide at bare and modified electrodes gave the peak potentials at about +210 and +110 mV, respectively. The over potential for the electrochemical oxidation of sulfide was found to shift by about 100 mV. These results indicate that PB/GCE in the BR buffer solution at pH 8.0 containing 0.1 M KCl performs a significant electrocatalytic effect towards sulfide oxidation.

The electrocatalytic oxidation of sulfide on the mediator modified electrode can be explained by the ECE mechanism.²³ According to this mechanism, the oxidized form of PB at the electrode surface firstly undergoes a reduction process with HS⁻ to produce reduced prussian white (PW). The reduced PB on the electrode surface in proportion to the amount of HS⁻ was then oxidized again. Finally, the anodic potential shifted to less positive potential.

and

Amperometric detection of sulfide in flow-injection system

The effects of some parameters on the amperometric response of PB/GCE towards sulfide in FIA system, such as the applied

Fig. 1 Cyclic voltammograms (10 cycles) of PB/GCE in a BR buffer solution (pH 8.0) containing 0.1 M KCl vs. Ag/AgCl at 50 mV/s.

Fig. 3 Cyclic voltammograms of PB/GCE: a) in the absence of sulfide, b) in the presence of 2 mM sulfide, c) bare GCE in the presence of 2 mM sulfide. BR buffer pH 8.0 containing 0.1 M KCl; scan rate, 50 mV/s.

Fig. 2 SEM image of: A) PB/GCE, B) bare GCE.

Fig. 4 Effect of the applied potential on amperometric peak currents of sulfide. a) bare GCE and b) PB/GCE (0.05 mM injected sulfide).

Fig. 5 Effect of the flow rate on the electrocatalytic current of sulfide.

potential, flow rate, sample loop and tubing length, were investigated and optimized by recording current-time curves of 0.05 mM sulfide.

Firstly, the current-time curves were recorded at various applied potentials for both PB/GCE and a bare electrode under the same conditions (flow rate, 1 mL/min; sample loop, 100 μ L; tubing length, 10 cm; flowing carrier stream, BR buffer solution pH 8.0 containing 0.1 M KCl). After a steady background current was obtained, a 0.05 mM sulfide solution was injected into the carrier stream to obtain current-time curves. Figure 4 shows a plot of the electrocatalytic currents derived from modified and bare electrodes vs. the applied potentials. The response currents for the electrocatalytic oxidation of sulfide at the modified electrode in the FIA system became apparent at -100 mV, and sufficient current was obtained at $+150$ mV, while the bare GCE had a significant lower current, which was increased by increasing the applied potential at $+300$ mV. The current values obtained from the modified electrode were 6.5-times higher than those obtained from the bare GCE at $+150$ mV. The results indicated that the optimum applied potential was $+150$ mV.

After optimization of the applied potential, the effect of the flow rate on the electrocatalytic oxidation of sulfide was

Fig. 6 FIA amperometric current-time curves of sulfide with various concentrations using PB/GCE. Carrier stream, BR buffer solution pH 8.0 containing 0.1 M KCl; applied potential, $+150$ mV; flow rate, 1.4 mL/min; sample loop, 100 μ L; transmission tubing length, 10 cm.

investigated by recording current-time curves at various flow rates using PB/GCE under the same conditions (applied potential, $+150$ mV; sample loop, 100 μ L; tubing length, 10 cm; flowing carrier stream, BR buffer solution pH 8.0 containing 0.1 M KCl; sulfide concentration, 50 μ M). The peak currents decreased with an increase of the flow rate in the range of 0.125 to 1 mL/min, then started to slightly increase at between 1 and 1.4 mL/min (Fig. 5). At flow rates higher than 1.6 mL/min, the peak currents slightly decreased. Although the highest peak currents were observed at low flow rates, very broad peaks were observed and the sample frequency was down significantly. Therefore, these flow rate values were not evaluated the optimum values. The flow rate of 1.4 mL/min was considered to be the optimal, since a significant narrower peak current and high sampling frequency was obtained by using this flow rate value.

As a result, the optimal applied potential, flow rate, sample volume and transmission tubing length for the amperometric detection of sulfide in flow injection system were chosen as $+150$ mV, 1.4 mL/min, 100 μ L and 10 cm, respectively (the sample volume and transmission tubing length obtained from our previous study).²² From these optimal conditions, amperometric currents vs. various concentrations of sulfide were also obtained using PB/GCE.

Figure 6 shows current-time curves for the amperometric FIA responses at various concentrations of sulfide. As can be seen from this figure, the electrocatalytic current increased linearly up to 100 μ M, and then the peak height did not increase linearly upon increasing the concentration after a higher concentration value than 100 μ M. In addition, the sensitivity seemed to be lowered when the sample concentration became high. Especially at concentrations higher than 300 μ M, degradation of the PB electrode surface may have occurred because the peak height considerably decreased in repeated measurements.

A linear relationship between the sulfide concentration and the peak current was obtained over the concentration range 5×10^{-7} – 1×10^{-4} M by the amperometric FIA method at the PB/GCE (Fig. 7).

The precision of the method was investigated by repeated injections ($n = 10$, 100 μ L) of the 1×10^{-5} M sulfide, and the relative standard deviation (RSD) was found to be 7.1%. The limit of detection (LOD) was calculated to be 3×10^{-7} M for an amperometric determination of sulfide in the FIA system.

Some analytical detection parameters, such as the detection potential of sulfide, linearity ranges and calculated LOD

Fig. 7 Calibration curve of sulfide.

obtained from PB/GCE, were compared with results obtained from our previous studies using MB,²² quercetin²³ and hematoxylin.²⁴ Although quercetin and hematoxylin modified pencil graphite electrodes (PGEs) allow a disposable, low cost, renewable sensor for sulfide determination, the electrocatalytic detection potential (DP) of sulfide at PB/GCE was found to be more negative than the DP of sulfide at quercetin and hematoxylin modified PGEs. The LOD of the proposed method is better than that obtained from a hematoxylin modified PGE. However, the LOD of the proposed method was the same as that obtained from the quercetin modified PGE; the linearity range of the quercetin modified PGE was better than that of PB/GCE. While the photoelectrocatalytic detection of sulfide in the FIA system using poly-MB modified GCE²² shows the same DP potential as the proposed method, its linearity range and LOD were better than that of the proposed method.

Sulfide determination in wastewater samples

The amperometric FIA method at the PB/GCE was also tested in wastewater samples taken from the influents and effluents of the Kepez municipal wastewater treatment plants (WWTP) in Canakkale, Turkey. It is known that such wastewater can possibly include interference compounds that may influence to sulfide determination. Therefore, a separation system similar to that proposed by Mousavi and Sarlack³² was used to transfer all of the sulfide content into H₂S form before being captured by a buffer solution. Then, the amount of sulfide was determined by the amperometric FIA system using the PB/GCE method. As we expected, the sulfide contents in the treated water samples were found to be very low, or undetectable, since most of the sulfide species in the municipal waste have been removed through chemical and biological operations used in WWTPs. The sulfide content in untreated and treated water samples were also studied with the MB spectroscopic method, which involves the reaction of aqueous sulfide with *N,N*-dimethyl-*p*-phenylenediamine in the presence of a catalyzer, FeCl₃. Although there is systematic error in the results for 16.05.2011 (treated) and 16.03.2012 (untreated), the other results confirmed that the sulfide measurements performed by PB/GCE in FIA system were in good agreement with those obtained from the MB spectroscopic method (Table 1), using t-test at the 95% confidence level. The accuracy of the method was also verified by recovering studies adding standard sodium sulfide solutions to the samples. Recoveries of 95 – 115% were obtained in this study.

Table 1 Sulfide measurements in different wastewater samples using PB/GCE and MB spectrophotometric method (*n* = 5)

Date	Sample	Amperometric method/ μ M	Reference method/ μ M
16.06.2011	U	639.6 $\pm$ 41.5	659.3 $\pm$ 52.4
	T	11.2 $\pm$ 0.9	13.4 $\pm$ 1.9
16.05.2011	U	64.6 $\pm$ 4.1	68.9 $\pm$ 5.6
	T	3.7 $\pm$ 0.3	4.7 $\pm$ 0.6
16.03.2012	U	37.4 $\pm$ 1.6	46.8 $\pm$ 1.9
	T	Undetectable	Undetectable

Sample: U, untreated wastewater; T, treated wastewater.

Conclusions

This study demonstrated that PB/GCE showed significant electrocatalytic activity towards sulfide oxidation. It was observed that the oxidation peak potential of sulfide shifted from +210 mV at a bare GCE to +110 mV at the PB/GCE. Besides, an enhancement in the oxidation peak current of sulfide was observed. The amperometric detection of sulfide with PB/GCE was successfully applied in the FIA system using a homemade electrochemical flow cell. The detection limit of sulfide was estimated to be 3×10^{-7} M in this study. It can be concluded that this paper shows the first study on the amperometric FIA determination of sulfide using a PB/GCE.

Acknowledgements

Y. D. and B. E. are grateful to the Scientific and Technological Research Council of Turkey TUBITAK (Project No. 210T112) for financial support.

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