

*Full Paper*

## **Electrocatalytic Oxidation of Sulfite and its Highly Sensitive Determination on Graphite Screen Printed Electrode Modified with New Schiff base Compound**

**Hamed Maaref, Mohammad Mehdi Foroughi,\* Enayatollah Sheikhsosseini, and Mohammad Reza Akhgar**

*Chemistry Department, Kerman branch, Islamic Azad University, Kerman, Iran*

\*Corresponding Author, Tel.: +98 34331321750

E-Mail: [mohammadmehdi869@yahoo.com](mailto:mohammadmehdi869@yahoo.com)

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**Abstract-** An electrochemical method for determination of sulfite has been developed using Schiff base modified graphite screen printed electrodes as a disposable chemosensor. The modified graphite screen printed electrode was characterized with voltammetry. Differential pulse voltammogram of modified SPE in the presence of sulfite showed a characteristic peak current at 350 mV. A linear response of the sensor was observed in the concentration range of 0.5-300.0  $\mu\text{M}$  of the analyte. The limit of detection (LOD) was found to be 0.3  $\mu\text{M}$  for sulfite. The method has been used for the determination of sulfite in the natural water samples. These analytical figures of merit evidence the outstanding performance of the modified electrode, which was also successfully applied to the determination of sulfite in environmental and biological samples.

**Keywords-** Sulfite, Schiff base, Voltammetric sensor, Graphite screen printed electrode, Real samples

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### **1. INTRODUCTION**

Sulfite is commonly used as a preservative in food, beverages and pharmaceuticals to prevent oxidation, bacterial growth, and control enzymatic reaction during production and storage [1,2]. Generally, the use of sulfite in normal conditions is not a problem for the

consumer but some people are sulfite-sensitive and nowadays, due to reported harmful effects [3], the sulfite content of food and beverages has been strictly controlled and limited by many countries [4]. For example, the United States Food and Drug Administration (US FDA) regulations have indicated that the sulfite ions in food and beverages should not exceed 10 ppm [2,5]. In Thailand, the Ministry of Public Health Thailand has prescribed levels of no more than 70 ppm. Therefore, a sensitive, selective, and fast method of determining sulfite is an important aspect of food quality control and safety.

The Association of Analytical Chemists (AOAC) has recommend a standard reference method for sulfite measurement, the Monier-Williams method, that involves a combination of distillation and titration [6]. However, the conventional titrimetric method suffers from poor precision and long analysis time and many alternative analytical methods have been developed for sulfite detection such as spectrophotometry [7-9], ion chromatography [10,11] and high-performance liquid chromatography [12].

However, these methods had high detection limit and low precision, thus development of more sensitive and reliable method is necessary. Electroanalytical techniques were proven to be relatively direct and effective for the detection of analytes [13-29]. Unfortunately, analytes exhibited high positive potential at bare carbon electrodes. Recently, various chemically modified electrodes (CMEs) have been prepared and applied in the determination of analytes, which can significantly lower the overpotentials and increase the oxidation current response [30-43].

Additionally, electrochemical techniques can also be used for the on-site analyses, as these instruments offer the benefits of portability, low cost, speed and simplicity. Since disposable screen-printed electrodes (SPEs) show advantages for field analysis as well as fast speed, high efficiency, portability, low cost and small sample size, these are promising sensors for chemical analytes [44,45]. Furthermore, chemical modification of the electrochemical sensors can be employed to produce specific and selective electrode for a definite target analytes [46-49]. Since, Schiff bases constitute an important class of electroactive compounds as they contain imine linkages. Therefore, Schiff bases can be used as electrode modifiers for the analysis of analytes [50].

Schiff bases are compounds having C=N double bond and formed by reaction of a primary amine and an aldehyde. Schiff bases are used as starting materials in the synthesis of important drugs such as antibiotics, antiallergics, antitumors and antifungals because of their biological activities [51,52]. They have also widely used as ligands in the field of coordination chemistry [53,54]. In addition, Schiff bases are important to synthesize the sensors for recognizing and sensing the materials, and to enlarge their areas of use [55,56].

In this work, a screen printed electrode modified with the new Schiff base compound (4,4'-(((methylenebis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene)) diphenol) was

used for sensitive voltammetric determination of sulfite and the modified electrode exhibited excellent electrocatalytic activity to sulfite.

## 2. EXPERIMENTAL

### 2.1. Chemicals and Apparatus

An Autolab potentiostat/galvanostat (PGSTAT 302N, Eco Chemie, the Netherlands) was employed to perform the electrochemical experiments and the system was controlled using a general purpose electrochemical system software (in Islamic Azad University Kerman branch).

IR spectrum was recorded on a FT-IR JASCO 680-PLUS spectrometer (20 spectra/sec,  $16\text{ cm}^{-1}$  resolution, MCT-W detector) using KBr pellets from  $4000\text{--}400\text{ cm}^{-1}$ . The  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR spectra were acquired using a Bruker 300 spectrometer which set at room temperature.

The screen-printed electrode (DropSens, DRP-110, Spain) consists of three conventional electrodes: graphite counter electrode, a silver pseudo-reference electrode and an unmodified graphite working electrode. pH was measured by a Metrohm 710 pH meter.

Sulfite and all other reagents were analytical grade, and were purchased from Merck (Darmstadt, Germany). For the preparation of buffers, the orthophosphoric acid and its salts were used to provide the pH range of 2.0–9.0.

### 2.2. Synthesis of 4,4'-(((methylenebis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))diphenol (4,4'-MPAMD)

4,4'-methylenedianiline (0.198 g) was added to EtOH (7 mL) solution of 4-hydroxybenzaldehyde (0.244 g). The mixture was stirred and refluxed for 92 h. Compound was obtained from the evaporation of EtOH. The as-obtained precipitates were centrifuged, and then washed with DI water and absolute ethanol for several times. The resulting products were dried in a vacuum oven at  $100\text{ }^\circ\text{C}$  for 12 h. Spectral data for this compound are given below:

4,4'-(((methylenebis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))diphenol (4,4'-MPAMD): IR (KBr,  $\text{cm}^{-1}$ ): 3445, 1580, 1511, 1447, 831.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$ : 6.88 (d,  $J=8.0$  Hz, 2H, H-Ar), 7.15 (d,  $J=8.0$  Hz, 2H, H-Ar), 7.25 (d,  $J=8.0$  Hz, 2H, H-Ar), 7.76 (d,  $J=8.0$  Hz, 2H, H-Ar), 8.45 (s, 2H, CH=), 10.1 (s, 2H, OH).  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )  $\delta$ : 115.5, 120.9, 127.6, 129.4, 130.5, 138.6, 149.9, 159.4, 160.4.

### 2.3. Preparation of the electrode

The bare screen-printed electrode was coated with 4,4'-(((methylenebis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))diphenol (4,4'-MPAMD) according to the following simple procedure. 1 mg 4,4'-MPAMD were dispersed in 1 mL aqueous solution within 45 min ultrasonication. Then, 5  $\mu$ l of the prepared suspension was dropped on the surface of carbon working electrodes. It remains at room temperature until becomes dry.

## 3. RESULT AND DISCUSSION

### 3.1. Spectral characterization

The FT-IR spectrum of 4,4'-MPAMD shown in Fig. 1. In this figure the broad peak at  $3445\text{ cm}^{-1}$  is attributed to O–H band, strong peak at  $1477$ ,  $1511$  and  $1580\text{ cm}^{-1}$  can be related to stretching vibration aromatic ring and imine band. The stretching band in  $831\text{ cm}^{-1}$  conformed para substitution aromatic rings.

The  $^1\text{H}$  NMR spectrum (Fig. 2) of the product showed singlet distinguished peak at  $\delta = 3.95$  ppm for methylene protons, four doublet peaks with  $J=8.0$  Hz for para substitution aromatic ring protons along two signals at  $\delta=8.45$  and  $10.11$  ppm for olefin and changeable OH protons respectively.

The  $^{13}\text{C}$  NMR spectrum (Fig. 3) revealed 9 distinct resonances at  $\delta=115.5$ - $160.4$  ppm in agreement with the product structure. It should be noted that methylene resonance is hidden in DMSO peaks.

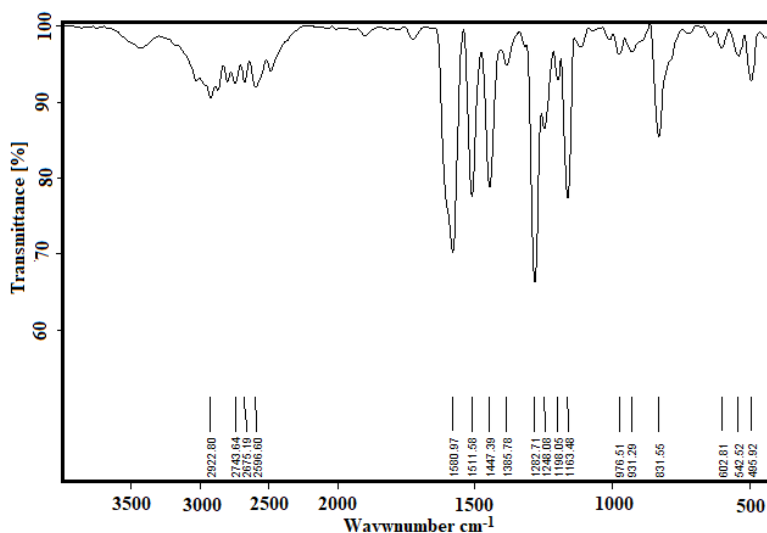
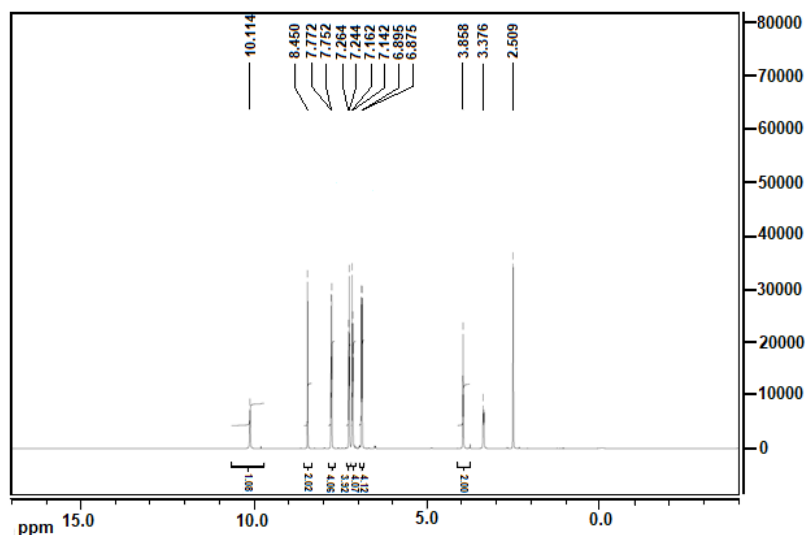
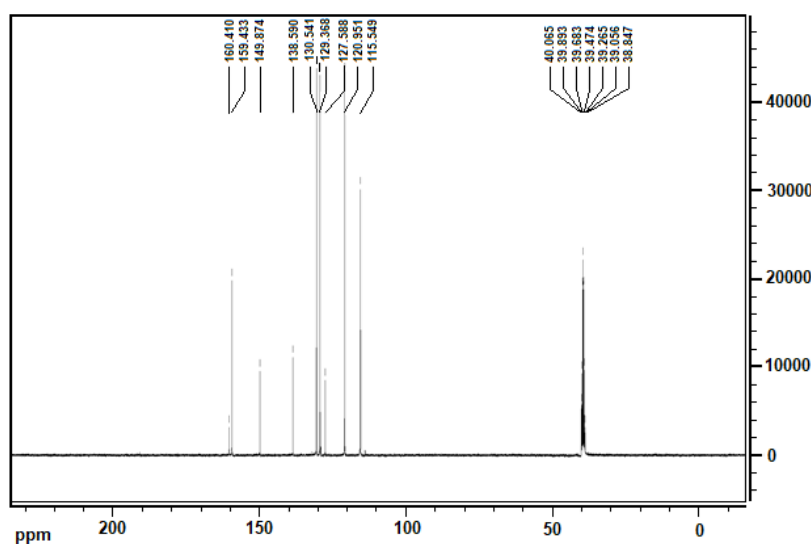


Fig. 1. FT-IR spectra of the 4,4'-MPAMD



**Fig. 2.**  $^1\text{H}$ NMR spectrum of the 4,4'-MPAMD at room temperature in DMSO



**Fig. 3.**  $^{13}\text{C}$ NMR spectrum of the 4,4'-MPAMD at room temperature in DMSO

### 3.2. Electrochemical properties of 4,4'-MPAMD/SPE

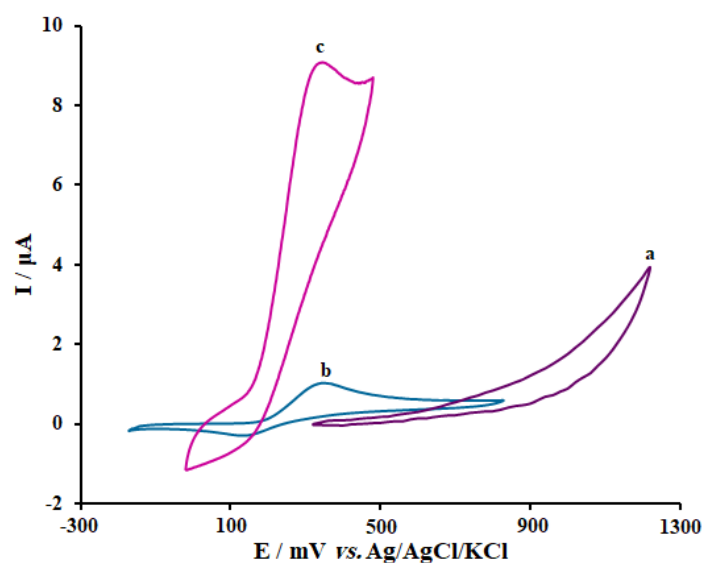
Given that our search did not reveal any published reports on the electrochemical and specifically the electrocatalytic activity of 4,4'-MPAMD in water, the electrochemical properties of 4,4'-MPAMD/SPEs were monitored in a PBS (pH=7.0) using cyclic voltametry. One advantage of 4,4'-MPAMD as an electrode modifier is its negligible solubility in water. Experiments resulted in reproducible and well-defined cyclic voltammograms with anodic and cathodic peaks at 0.35 and 0.13 V *vs.* Ag/AgCl/KCl (3.0 M), with a  $\Delta E_p = (E_{pa} - E_{pc})$  of 215 mV which is greater than the  $59/n$  mV expected for reversible system [57]. This could

suggest that the redox 4,4'-MPAMD couple in 4,4'-MPAMD/SPE behaves quasi-reversibly in an aqueous medium [57].

### 3.3. Electrochemical profile of the sulfite on the 4,4'-MPAMD/SPE

The electrochemical profile of sulfite greatly depends on the pH of the solution, which is not the case with the properties of the Fc/Fc<sup>+</sup>. Consequently optimizing the pH is critical while studying the electrocatalytic oxidation of sulfite, and hence the CV studies were conducted in a 0.1 M PBS solutions having different pH values in the range of 2.0-9.0 using the 4,4'-MPAMD/SPE. The results proved that the electrocatalytic oxidation of sulfite in such a system was more favored under neutral pH regimes, which is reflected by the gradual growth in the anodic peak current and the parallel decrease of the cathodic peak currents. Based on the observations, the pH of the test solutions were set at 7.0 as the optimal value.

The obtained cyclic voltammograms in the presence of 100.0  $\mu\text{M}$  sulfite using the 4,4'-MPAMD/SPE (Curve a) and bare SPE (Curve b) are shown in Fig. 4. According to CV results the maximum oxidation of sulfite on the 4,4'-MPAMD/SPE occurs at 350 mV which is about 870 mV more negative compared with unmodified SPE.

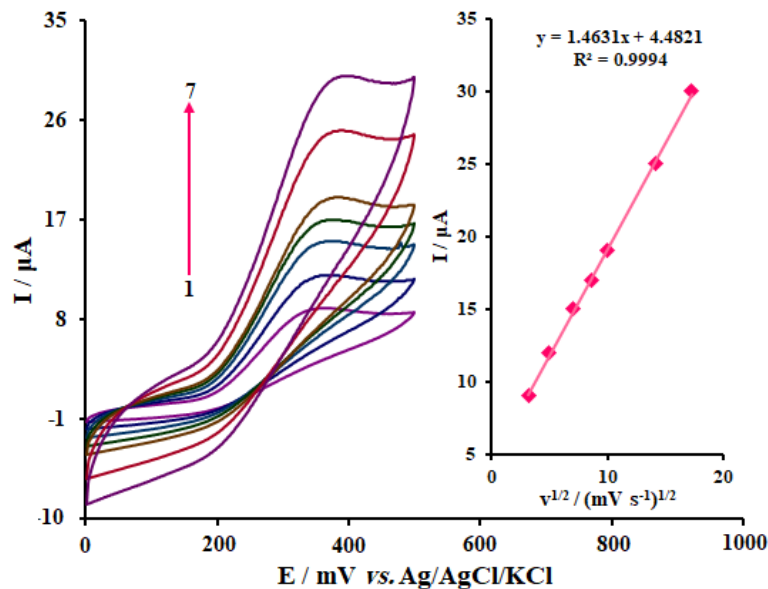


**Fig. 4.** Cyclic voltammograms of (a) bare SPE in 0.1 M PBS (pH 7.0) in the presence of 100.0  $\mu\text{M}$  sulfite, (b) 4,4'-MPAMD/SPE in 0.1 M PBS (pH 7.0) and (c) 4,4'-MPAMD/SPE in 0.1 M PBS (pH 7.0) in the presence of 100.0  $\mu\text{M}$  sulfite at the scan rate 50  $\text{mVs}^{-1}$

### 3.4. Effect of scan rate on the results

Increasing in scan rate leads to enhanced oxidation peak current according to the obtained results from the study of the effect of potential scan rates on the oxidation currents of sulfite,

Fig. 5. In addition, there is a linear relationship between  $I_p$  and the square root of the potential scan rate ( $v^{1/2}$ ) that demonstrates that the oxidation procedure of analyst is in control of diffusion (Fig. 3).



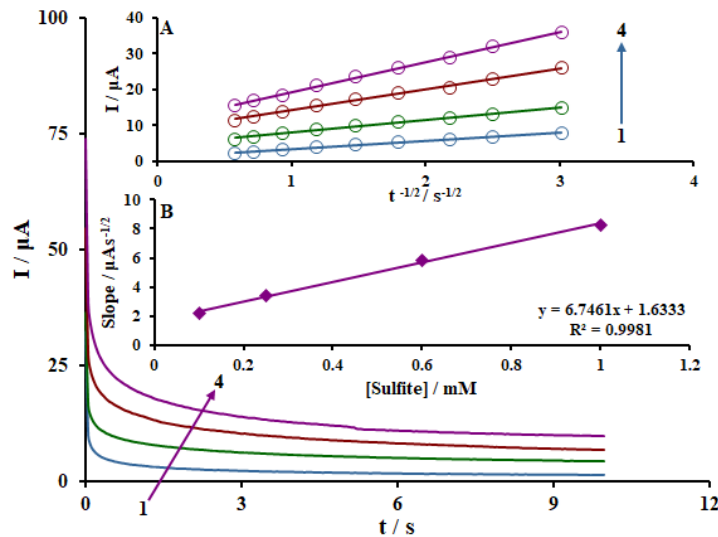
**Fig. 5.** Cyclic voltammograms of 4,4'-MPAMD/SPE in 0.1 M PBS (pH 7.0) containing 100.0  $\mu\text{M}$  sulfite at various scan rates; numbers 1-7 correspond to 10, 25, 50, 75, 100, 200 and 300  $\text{mV s}^{-1}$ , respectively. Inset: Variation of anodic peak current vs.  $v^{1/2}$

### 3.5. Chronoamperometric analysis

The analysis of chronoamperometry for sulfite samples was performed by use of 4,4'-MPAMD/SPE vs. Ag/AgCl/KCl (3.0 M) at 0.4 V. The Chronoamperometric results of different concentration of sulfite sample in PBS (pH 7.0) are demonstrated in Fig. 6. The Cottrell equation for chronoamperometric analysis of electroactive moieties under mass transfer limited conditions is as follow [57]:

$$I = nFAD^{1/2}C_b\pi^{-1/2}t^{-1/2}$$

Where  $D$  represents the diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ ), and  $C_b$  is the applied bulk concentration ( $\text{mol cm}^{-3}$ ). Experimental results of  $I$  vs.  $t^{-1/2}$  were plotted in Fig. 6A, with the best fits for different concentrations of sulfite. The resulted slopes corresponding to straight lines in Fig. 6A, were then plotted against the concentration of sulfite (Fig. 6B). The mean value of  $D$  was determined to be  $3.87 \times 10^{-6} \text{ cm}^2/\text{s}$  according to the resulting slope and Cottrell equation.

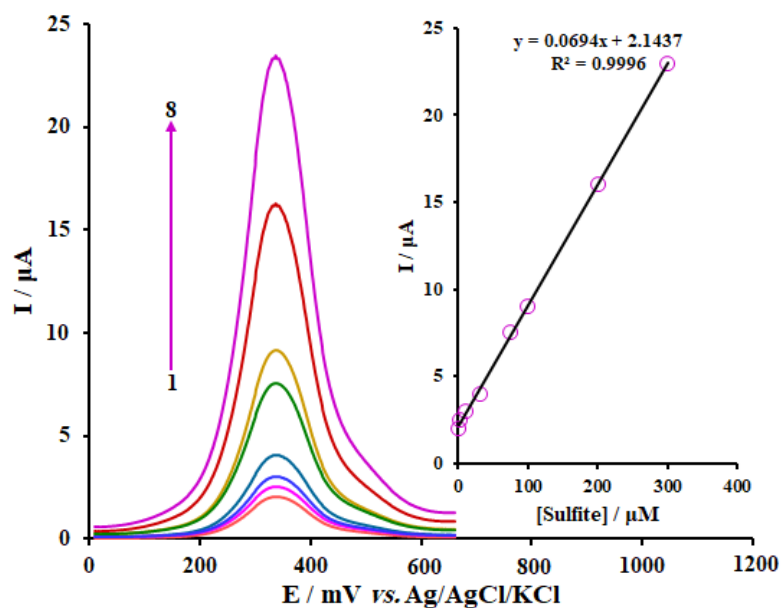


**Fig. 6.** Chronoamperograms obtained at 4,4'-MPAMD/SPE in 0.1 M PBS (pH 7.0) for different concentration of sulfite. The numbers 1–4 correspond to 0.1, 0.25, 0.6, and 1.0 mM of sulfite. Insets: (A) Plots of  $I$  vs.  $t^{-1/2}$  obtained from chronoamperograms 1–4. (B) Plot of the slope of the straight lines against sulfite concentration

### 3.6. Calibration curves

Based on the resulting peak currents of sulfite by use of 4,4'-MPAMD/SPE, the quantitative analysis of two targets were done in water solutions (Initial potential=0.09 V, End potential=0.66 V, Step potential=0.1 V, Modulation amplitude=0.02505 V). The modified electrode (4,4'-MPAMD/SPE) as working electrode in the range of sulfite concentration in 0.1 M PBS was used in differential pulse voltammetry (DPV) due to the advantages of DPV including the improved sensitivity and better performance in analytical applications (Fig. 7). According to the results, a linear relationship exists between the peak currents and concentrations of sulfite within the concentration range of 0.5–300.0  $\mu\text{M}$  with the correlation coefficient of 0.9996 (Fig. 7). The detection limit was obtained 0.3  $\mu\text{M}$ . Table 1. shows a comparison of the analytical figures of merit of the proposed method with electrochemical techniques for the determination of sulfite.





**Fig. 7.** DPVs of 4,4'-MPAMD/SPE in 0.1 M (pH 7.0) containing different concentrations of sulfite. Numbers 1–12 correspond to 0.5, 2.5, 10.0, 30.0, 75.0, 100.0, 200.0 and 300.0  $\mu\text{M}$  of sulfite. Inset: Plot of the electrocatalytic peak current as a function of sulfite concentration in the range of 0.5-300.0  $\mu\text{M}$

**Table. 1.** Comparison of some electrochemical procedures used in the determination of sulfite

Electrode	Linear Range	Detection Limit	Ref.
Carbon paste electrodes modified with gold nanoparticles and $\text{Si}_4\text{Pic}^+\text{Cl}^-$	2.54-48.6 $\text{mg L}^{-1}$	0.88 $\text{mg L}^{-1}$	[58]
Glassy carbon electrodes modified with films of Prussian Blue	0.0-40.0 mM	80.0 $\mu\text{M}$	[59]
Glassy carbon electrode modified with electropolymerized Co(II) meso-tetrakis (2-thienyl)porphyrin	0.1-5000.0 $\mu\text{M}$	-	[60]
Paraffin impregnated graphite electrode modified with nickel aquapentacyanoferrate	2.78-3000.0 $\mu\text{M}$	0.926 $\mu\text{M}$	[61]
Graphite screen printed electrode modified with 4,4'-(((methylenebis(4,1-phenylene))bis(azanylylidene))bis(methanylylidene))diphenol	0.5-300.0 $\mu\text{M}$	0.3 $\mu\text{M}$	This Work

### 3.7. Analysis of real samples

The applicability of this modified electrode in the determination of real samples was assessed through the determination of sulfite in water sample using the described method. In order to perform this analysis, standard addition method was employed and the results are listed in Table 2. Accordingly, the results of sulfite recovery are satisfactory and the reproducibility of the results is proved by the mean relative standard deviation (R.S.D.).

**Table 2.** The application of 4,4'-MPAMD/SPE for determination of sulfite in water samples (n=5). All concentrations are in  $\mu\text{M}$

Sample	Spiked	Found	Recovery (%)	R.S.D. (%)
Well water	0	-	-	-
	10.0	9.9	99.0	3.2
	15.0	15.2	101.3	1.6
	20.0	20.4	102.0	2.3
	25.0	24.3	97.2	2.7
River water	0	-	-	-
	7.5	7.6	101.3	1.8
	12.5	12.2	97.6	2.7
	17.5	17.9	102.3	2.1
	22.5	22.6	100.9	3.1

## 4. CONCLUSION

Sulfite was determined electrochemically by differential pulse voltammetry using Schiff base modified graphite screen printed electrode. Redox characteristics of the modified electrode showed distinct and well-defined peaks corresponding to Schiff base. Modified electrode is sensitive for sulfite in the concentration range 0.5-300.0  $\mu\text{M}$  with limit of detection (LOD) 0.3  $\mu\text{M}$ . The proposed chemosensor can be used for on-site detection of sulfite in different water samples.

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