



Original scientific paper

## Voltammetric determination of cysteamine at the surface of a quinizarine/Bi<sub>2</sub>S<sub>3</sub> nanorod-modified carbon paste electrode

Shaimaa Sabte Mutlak<sup>1</sup> , Hussein Abd Aljabbar Ismael<sup>2</sup> , Hasan Ali Alsailawi<sup>3</sup> ✉ and Banaz Salih Ahmed<sup>4</sup>

<sup>1</sup>Department of Basic Science, College of Dentistry, University of Baghdad, Iraq

<sup>2</sup>College of Medicine, University of Al-Ameed, Karbala, Iraq

<sup>3</sup>Department of Basic Sciences, College of Dentistry, University of Kerbala, 56001, Karbala, Iraq

<sup>4</sup>AL-Zahraa University for Women, College of Pharmacy, Iraq

Corresponding Author: [hasanali.alsailawi@gmail.com](mailto:hasanali.alsailawi@gmail.com)

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### Abstract

Bi<sub>2</sub>S<sub>3</sub> nanorods and quinizarine (QZ) were used to chemically modify a carbon-paste electrode (CPE) (QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE). This was employed as an electrochemical sensor to measure trace levels of cysteamine (CYST). Because of a significant reduction in anodic overpotentials, QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE demonstrated effective electrocatalytic activity for the oxidation of CYST. Using differential pulse voltammetry, the linear range of CYST concentration under ideal conditions was 0.5 to 500.0 μM, and the detection limit was 0.1 μM. The modified CPE was used to determine CYST in urine and pharmaceutical samples.

### Keywords

Transition metal sulphide; cystinosis; aminothiols; chemically modified electrode

### Introduction

Many researchers are drawn to metal sulphides (MS), mainly because of their high theoretical specific capacitance and superior reaction-rate ability [1]. As an excellent electrode material, MS looks promising for electrocatalysis [1]. For instance, supercapacitors have employed molybdenum sulphide [2], nickel sulphide [3], titanium sulphide [4] and bismuth sulphide [5]. Bismuth sulphide (Bi<sub>2</sub>S<sub>3</sub>) has a high theoretical capacity due to its narrow band gap, which provides excellent electrical conductivity and effective carrier transport characteristics [5].

Cysteamine (CYST), an aminothiols molecule, is used to treat cystinosis [6]. A series of long-term clinical studies suggests that CYST therapy (administered as CYST hydrochloride) helps stabilize renal function; it also slows down glomerular degeneration and supports steady linear growth [7]. Numerous cell culture and animal models have demonstrated the neuroprotective properties of CYST [7]. Determining this medication is therefore crucial for pharmaceutical and biological molecules.

Several techniques were previously employed for analytical determination of CYST using fluorescence [8], capillary electrophoresis [9], high-performance liquid chromatography (HPLC) [10,11], and electrochemistry [12,13]. Recently, electrochemical techniques have attracted increasing interest because of their simplicity and short analysis time compared with conventional methods.

In electrochemical sensing, substrate electrode selection plays an important role in achieving sensitivity and stability [14]. Glassy carbon electrodes (GCEs), screen-printed electrodes (SPEs), and boron-doped diamond (BDD), have been employed, but the carbon paste electrode (CPE) is particularly promising for drug determination [15]. CPEs can readily renew the surface under the same conditions, whereas GCEs or BDDs must undergo long, harsh mechanical polishing to remove surface passivation caused by adsorption of CYST oxidation products [16].

Additionally, as the composite matrix, CPE can incorporate a modifier throughout the electrode body, providing a stable, uniformly distributed modifier rather than one confined to the film surface, where it is more likely to detach [17].

The low background current, low cost, and chemical biostability of CPEs also make them a good platform for designing stable sensors in various complex environmental samples [17]. Nevertheless, direct oxidation of CYST on bare CPE has been accompanied by poor electron-transfer kinetics, surface passivation, and low sensitivity [16]. To address these limitations, modifying CPE with nanostructured materials and mediators has been shown to enhance electrocatalytic activity, adsorption capacity, and analytical performance [18,19].

Therefore, in this work, we describe the construction and applicability of quinizarine/Bi<sub>2</sub>S<sub>3</sub> nanorod-modified CPE (QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE) as a novel electrode for CYST measurement and electrocatalysis in a buffer solution. Next, we assessed the modified electrode's analytical performance in measuring CYST in actual samples.

## Experimental

### *Chemicals and apparatus*

We used a computerized potentiostat/galvanostat, Autolab type III (Eco Chemie B.V.A.). An Ag/AgCl/KCl, platinum wire and QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE were used as the reference, auxiliary and working electrodes. Every solution was made fresh using twice-distilled water. Fluka provided the CYST and QZ, which were used exactly as supplied.

Additional reagents were of analytical grade (Merck). Graphite pastes were bound using paraffin oil (DC 350, Merck) and graphite fine powder (Merck). Orthophosphoric acid and its salts were used to create buffer solutions (PBS) with pH values between 2.0 and 9.0.

### *Synthesis of Bi<sub>2</sub>S<sub>3</sub> nanorods*

The hydrothermal technique was used to create the Bi<sub>2</sub>S<sub>3</sub> NRs. First, 35 mL of deionised water was stirred for 10 minutes to fully dissolve 0.4110 g of thiourea (5.40 mmol). The solution was stirred while 0.6111 g Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (1.26 mmol) was added. The solution was stirred for 1 hour. The combined solution was then transferred to an autoclave, heated to 200 °C for 15 hours, and allowed to cool. The precipitates were then collected and dried for 15 hours at 67 °C.

### *Preparation of electrode*

QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPEs were prepared by hand-mixing 10 mg of QZ with 95× its weight of graphite powder and 4× its mass of Bi<sub>2</sub>S<sub>3</sub> NRs. After that, paraffin was poured into the blend and mixed for 20 min, evenly moistened paste, not clumpy or anything. The resulting paste was then packed into

the tip end of a glass tube ( $\sim 3.4$  mm inner diameter). The QZ-modified CPE (QZ/CPE) and the  $\text{Bi}_2\text{S}_3$  NRs-based CPE ( $\text{Bi}_2\text{S}_3$  NRs/CPE) were prepared using the same procedure, except without  $\text{Bi}_2\text{S}_3$  NRs in the first case and without QZ in the second. For comparison, an unmodified CPE was produced in the same manner but without adding QZ or  $\text{Bi}_2\text{S}_3$  NRs to the mixture, and it was used alongside the modified pastes.

### Real samples

Immediately after collecting the urine samples, a 10 mL portion was centrifuged at 3000 rpm for 15 min. Next, the upper layer was diluted 1:10 with PBS. Without further steps, the liquid was transferred to a voltammetric cell and measured.

For the CYST capsules, five units of cysteamine (150 mg *per* capsule) were fully homogenized, then 100 mg was dissolved in water by ultrasonication, specifically in 20 mL. The mixture was filtered; the filtrate was transferred to a 100-mL volumetric flask and diluted to the calibration line with PBS. The prepared sample was combined with varying CYST levels, and measurements were repeated.

## Results and discussion

### Electrochemistry of quinizarine / $\text{Bi}_2\text{S}_3$ nanorod-modified carbon paste electrode

QZ is only slightly soluble in water, so it can be added to the carbon paste. Thus, QZ can be added reproducibly by chemically modifying the electrode, and this step seems to work quite consistently.

First, the electrochemical profile of the QZ/ $\text{Bi}_2\text{S}_3$  NRs/CPE was checked by cyclic voltammetry (CV), Figure 1. The results show anodic peak potential,  $E_{\text{pa}} = 0.560$  V; cathodic peak potential,  $E_{\text{pc}} = 0.400$  V and  $\Delta E_p = 160$  mV.

CVs for the QZ/ $\text{Bi}_2\text{S}_3$  NRs/CPE were recorded at various scan rates (Figure 1).

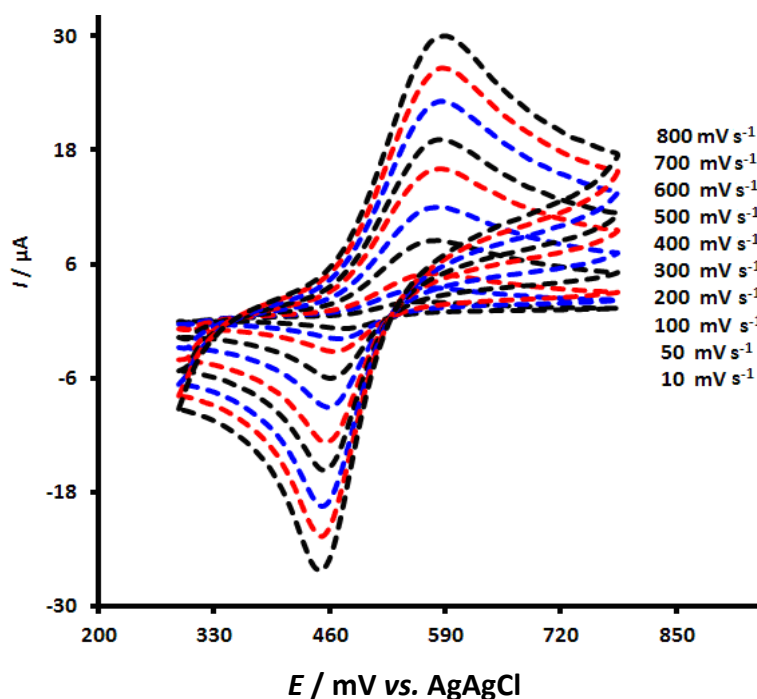


**Figure 1.** CVs of QZ/ $\text{Bi}_2\text{S}_3$  NRs/CPE in PBS at various scan rates

Figure 2A shows that the peak currents,  $I_p$ , show a relation with scan rate ( $v$ ). There is also another linear correlation between the peak currents and the potential sweep rate, which suggests the redox reaction is not limited by diffusion, or at least not mainly driven by it. Then Figure 2B presents the

anodic peak potentials,  $E_p$ , versus the sweep rate. When scan rates exceed 500 mV s<sup>-1</sup>, the  $E_p$  values follow a linear trend with the logarithm of  $v$ . In those circumstances, the apparent charge transfer rate constant ( $k_s$ ) can be determined using Equation (1) [21]:

$$\log k_s = \alpha \log (1-\alpha) + (1-\alpha) \log \alpha - \log (RT/nFv) - \alpha(1-\alpha)nF\Delta E_p/2.3RT \quad (1)$$

where  $\alpha$  is the transfer coefficient,  $(1-\alpha)n_\alpha = 0.5$ , and the number of electrons ( $n$ ) is 2.  $k_s = 3.9$  s<sup>-1</sup> was obtained. The slopes shown in the plots in Figure 2B can be used to determine  $\alpha_c$  and  $\alpha_a = 1-\alpha_c$ . The evaluated values for the coefficients  $\alpha_c$  and  $\alpha_a$  are 0.5.

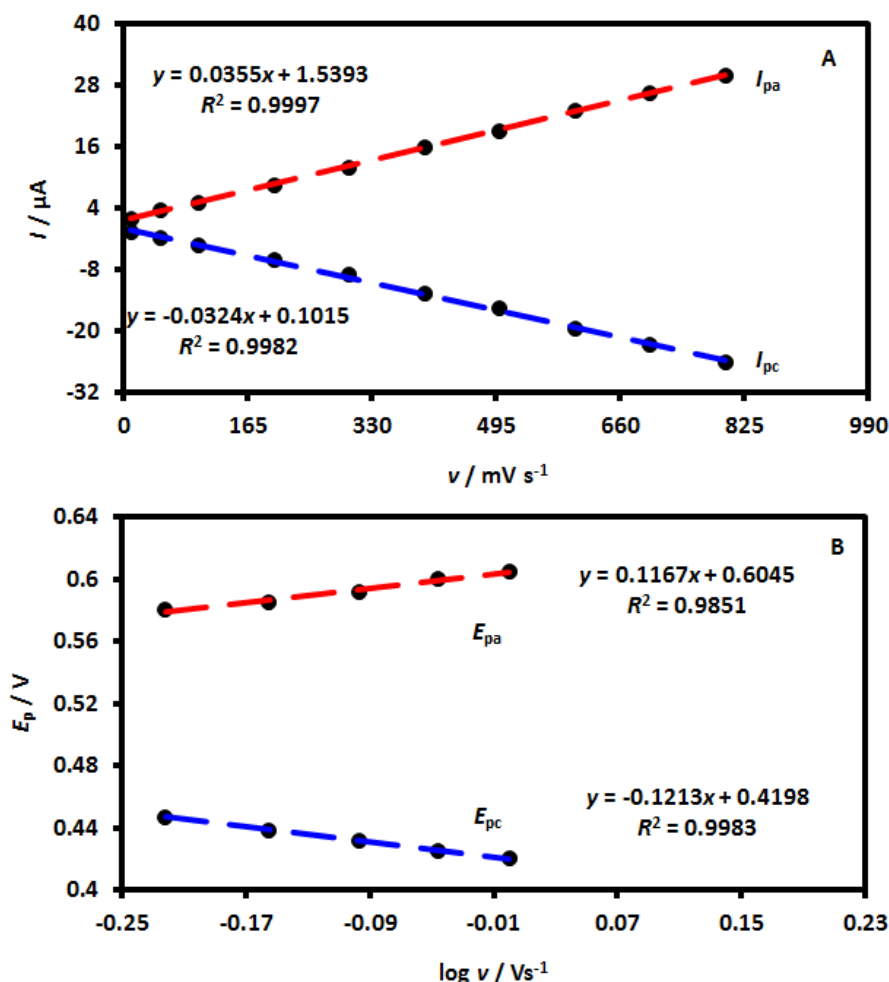


**Figure 2.** (A) Variations of  $I_p$  vs. scan rates. (B) Variation of  $E_p$  vs. the logarithm of the higher scan rates for QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE in PBS

#### Electrocatalytic oxidation of cysteamine at quinizarine /Bi<sub>2</sub>S<sub>3</sub> nanorod-modified carbon paste electrode

Figure 3 shows the CV responses for 30.0  $\mu M$  CYST at QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE, QZ/ CPE, Bi<sub>2</sub>S<sub>3</sub> NRs/CPE, and unmodified CPE. In general, the peak potential for CYST oxidation at QZ/ Bi<sub>2</sub>S<sub>3</sub> NRs/CPE and QZ/CPE is around 560 mV, while at Bi<sub>2</sub>S<sub>3</sub> NRs/CPE it is near 770 mV. At unmodified CPE, it was approximately 860 mV for CYST.

These data indicate that the most favourable electrocatalytic effect for CYST oxidation was achieved on QZ/Bi<sub>2</sub>S<sub>3</sub>NRs/CPE. For instance, the peak potential at QZ/Bi<sub>2</sub>S<sub>3</sub>NRs/CPE shifted by roughly 210 and 320 mV in the more negative direction compared with Bi<sub>2</sub>S<sub>3</sub> NRs/CPE and unmodified CPE.

Similarly, comparing the oxidation behaviour of CYST at QZ/CPE with that at QZ/ Bi<sub>2</sub>S<sub>3</sub> NRs/CPE shows a sharp increase in anodic peak current at QZ/ Bi<sub>2</sub>S<sub>3</sub> NRs/CPE compared with QZ/CPE. Overall, the data are straightforward and clearly indicate that Bi<sub>2</sub>S<sub>3</sub> NRs, together with the mediator (QZ), improve CYST oxidation.

In detail, the QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE, tested in PBS and, importantly, without CYST, showed a decent, well-behaved redox response. After adding 30.0  $\mu$ M CYST, the anodic peak current increased markedly.

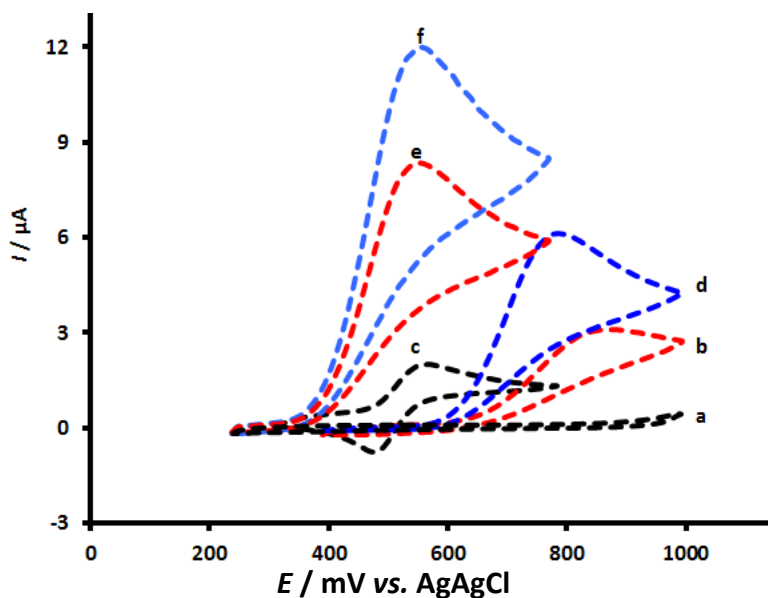


**Figure 3.** CVs of (a) CPE in PBS at  $10 \text{ mV s}^{-1}$  and (b) as (a) +  $30.0 \mu\text{M}$  CYST; (c) as (a) and (d) as (b) at the surface of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE and Bi<sub>2</sub>S<sub>3</sub> NRs/CPE, respectively. Also, (e) and (f) as (b) at the QZ/CPE and QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE, respectively.

#### Effect of scan rate

CV was employed to examine how scan rate affects oxidation of CYST on QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE (see Figure 4). As the scan rate increases,  $E_p$  shifts toward more positive values, as shown in Figure 4, suggesting a kinetic limitation for the electrochemical process. Moreover, when a linear plot of peak current ( $I_p$ ) against the square root of scan rate ( $v^{1/2}$ ) is made, it was found to work in the 10 to  $100 \text{ mV s}^{-1}$  range, meaning the mechanism is more diffusion-controlled rather than being purely surface-governed, especially at sufficient overpotential (Figure 4 inset).

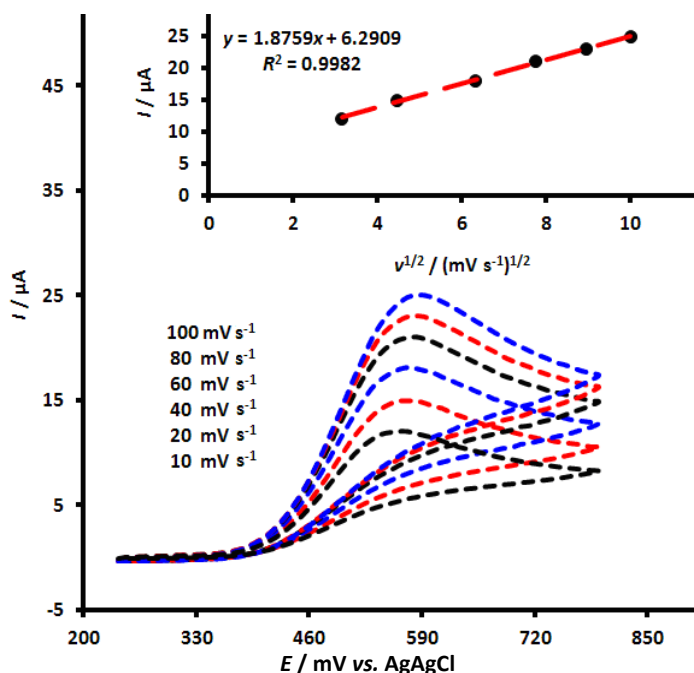


**Figure 4.** CVs of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE at different scan rates in PBS with  $30.0 \mu\text{M}$  CYST. Inset: Variations of anodic peak current vs.  $v^{1/2}$

### Calibration plot and limit of detection

The concentration of CYST was measured using DPV (Figure 5). Two linear segments in the concentration range of 0.5 to 30.0  $\mu\text{M}$  (Figure 6A) and 30.0 to 500.0  $\mu\text{M}$  (Figure 6B) made up the peak current vs. CYST concentration plot. It was discovered that the CYST detection limit ( $3\sigma$ ) was 0.1  $\mu\text{M}$ .

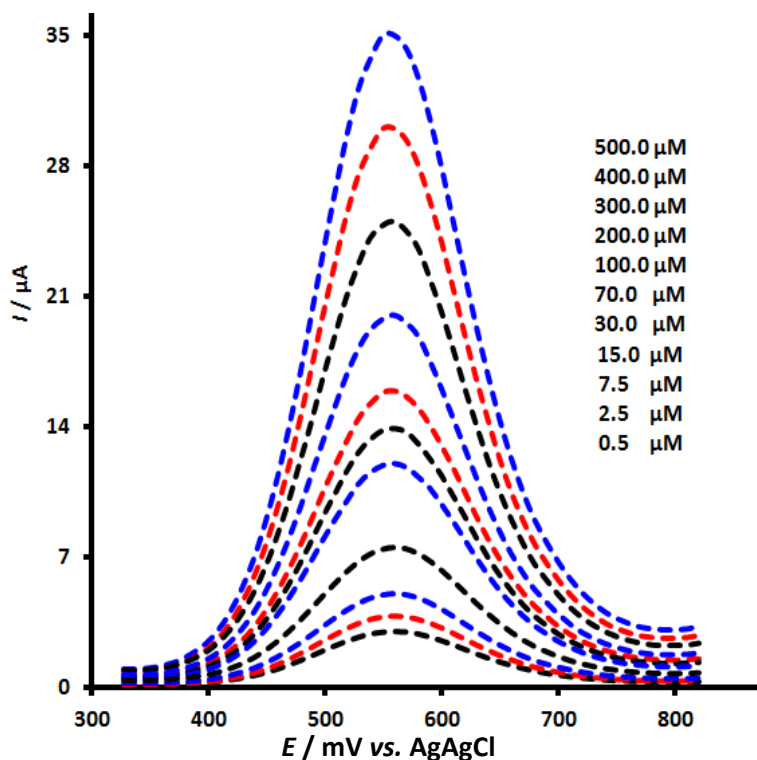


Figure 5. DPVs of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE in PBS with varying amounts of CYST

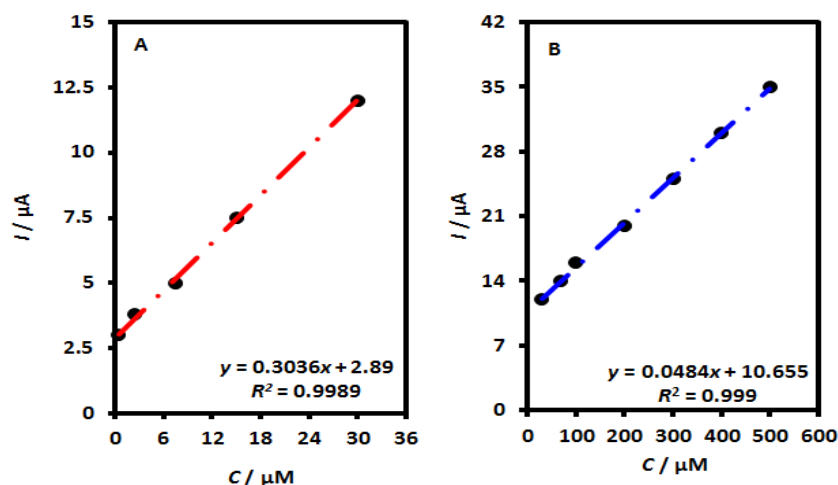


Figure 6. Calibration plots for CYST concentration in the range of 1.0 to 20.0  $\mu\text{M}$  (A) and 20.0 to 800.0  $\mu\text{M}$  (B)

### Stability and repeatability of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE

We assessed the stability and repeatability of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE over three weeks. The experiments were repeated after modifying the electrode, then storing it in the environment for three weeks. The CVs showed no change in the peak potential for CYST, except for a decrease of less than 2.5 % compared with the first reaction.

Voltammograms were recorded in the presence of CYST after being cycled twelve times. The results showed that QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE reduced fouling by the analyte and related oxidation products, while peak potentials remained the same and currents decreased by less than 2.2 %.

### Analysis of real samples

The systematic feasibility of the suggested approach was assessed by quantifying CYST in the capsule and urine specimens using the standard addition approach. Table 1 shows the CYST determination outcomes in systematic capsule urine samples. The test results demonstrated CYST recoveries that were satisfactory. The mean relative standard deviation (RSD) was used to examine the reproducibility of the approach. The systematic dosage in the capsule was 1510.3 mg *per* capsule. The nominal value on the capsule label (150.0 mg *per* capsule) and the results from the QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE did not differ significantly.

**Table 1.** Voltammetric determination of CYST in real specimens at QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE. (n = 5)

| Sample       | Amount, $\mu\text{M}$ |       | Recovery, % | RSD, % |
|--------------|-----------------------|-------|-------------|--------|
|              | Added                 | Found |             |        |
| CYST capsule | 0                     | 6.9   | -           | 2.2    |
|              | 1.0                   | 7.8   | 98.7        | 3.3    |
|              | 2.0                   | 9.1   | 102.2       | 2.1    |
|              | 3.0                   | 9.8   | 99.0        | 1.9    |
|              | 4.0                   | 11.3  | 103.7       | 2.8    |
| Urine        | 5.5                   | 5.6   | 101.8       | 2.6    |
|              | 7.5                   | 7.2   | 96.0        | 3.4    |
|              | 9.5                   | 9.4   | 98.9        | 2.0    |
|              | 11.5                  | 11.9  | 103.5       | 2.3    |

### Conclusions

In this article, a CPE modified with Bi<sub>2</sub>S<sub>3</sub> nanorods and quinizarine was constructed and used for the study of the electrochemical behaviour of CYST. CYST electrooxidation is catalysed, according to the electrochemical behaviour of CYST at the surface of QZ/Bi<sub>2</sub>S<sub>3</sub> NRs/CPE. Finally, we investigated the modified electrode as a simple, accurate, and selective electrochemical sensor for determining CYST in real samples.

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