



Full Length Article

Determination of thiol content in fossil fuel by cyclic voltammetry using *in situ* Bismuth film electrode



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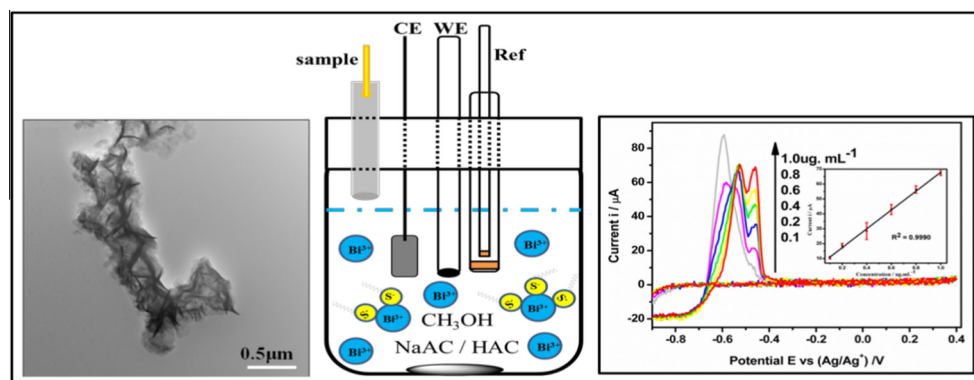
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HIGHLIGHTS

- Thiol in fuel detected by CV using *in situ* BiFE in HAC-NaAc/methanol electrolyte.
- An extra anodic peak appeared due to the adsorbed thiols on Bi film.
- The intensity of extra peak at -0.45 V is proportional to the thiol concentration.
- The proposed method can be applied for on-site analysis of thiol in fuel.
- The sensor is fast, sensitive, accurate and environment-friendly.

GRAPHICAL ABSTRACT

A fast and environment-friendly strategy for the direct determination of thiol in fossil fuel by cyclic voltammetry (CV) method using an *in situ* Bismuth film electrode (BiFE) in an acetic acid-acetate/methanol electrolyte is reported. An extra anodic peak in the CV curve appears except for the peak due to the dissolution of Bi film. The intensity of the extra anodic peak at -0.45 V is proportional ($R^2 \geq 0.9990$) to the thiol concentration in the electrolyte over the range of 0.10 – 1.00 $\mu\text{g mL}^{-1}$ with the sensitivity of 121.35 $\mu\text{A } \mu\text{g}^{-1}$ mL. The proposed method has been successfully applied to determination of thiol in fuel samples with satisfactory recoveries 100.60 – 110.00% .



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ABSTRACT

A fast and environment-friendly strategy for the determination of thiol content in fossil fuel by cyclic voltammetry (CV) method using an *in situ* Bismuth film electrode (BiFE) with an acetic acid-acetate/methanol electrolyte is reported. An extra anodic peak in the CV curve appears, which is at a more positive potential than the oxidation of normal Bi atoms due to the oxidation of Bi adsorbed by thiol. In addition, the cathodic peak is positively shifted due to overlap of the reduction peaks of the Bi^{III} ions and the Bi^{III}/thiol complex, forming a Bi film. It is demonstrated that the intensity of the extra anodic peak at -0.45 V is proportional ($R^2 \geq 0.9990$) to the thiol concentration in the electrolyte over the range of 0.10 – 1.00 $\mu\text{g mL}^{-1}$ with a sensitivity of 121.35 $\mu\text{A } \mu\text{g}^{-1}$ mL. The proposed method has been successfully applied to the determination of thiol contents in fuel samples with satisfactory recoveries of 100.60 – 110.00% .

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1. Introduction

Sulfur content in fossil fuel (gasoline and diesel) has attracted considerable attention in recent years due to growing concerns about SO₂ emissions resulting from the combustion of fossil fuel [1–3]. Many countries and organizations have restricted the content of sulfur in fossil fuel, such as the worldwide fuel charter established from 2006 to 2012. Advances in fuel desulfurization technology have established that efficient desulfurization is dependent on the type and content of sulfur compounds in the fuel [4]. For example, the Merox process developed by Universal Oil Products Company is a special process for eliminating thiol compounds in crude oil [5–7]. However, the majority of analytical techniques are focused on determining total sulfur content [8,9] based on the amount of SO₂ after combustion. While there are a few methods available for the direct measurement for certain sulfur-containing compounds (mainly thiol) based on separation (such as gas chromatography/mass spectrometry [10], colorimetry [11], titration [12,13] and X-ray fluorescence spectrometry [14]), these methods seldom satisfy the demands of accuracy and rapidity in analyzing sulfur compounds for desulfurization technologies.

Electrochemistry is reported to be a rapid and selective method for the analysis of thiol content based on the exclusive reaction between mercapto groups and the electrode surface, such as the formation of thio-metal bonds (Au–S [15–17], Hg–S [18–20], Cu–S [21] or Bi–S [22,23]). Mercury electrode (ME) have also been used in the analysis of thiol based on the well-defined anodic peak assigned to the formation of Hg(RS)₂ [18]. The intensity of this peak is proportional to the concentration of thiol. However, the application of mercury electrode is limited due to their toxicity and poor linear range. In contrast, bismuth film electrode (BiFE) is proposed to be environmentally friendly, nontoxic and low cost materials for electrochemical analyses [24–28]. BiFE has been used in the detection of thiol at low concentrations in aqueous solutions such as homocysteine, cysteine and *n*-acetyl cysteine [29,30].

However, direct detection of thiol in fuel by BiFE has not yet been reported. This could be due to the poor conductivity of fuel and the instability of the pre-plating process for BiFE in non-aqueous electrolyte, where the anodic stripping potential of the thiol is more positive than Bi [22,31]. In this study, thiol in fuel is directly detected using cyclic voltammetry and *in situ* BiFE in acetic acid-acetate/methanol electrolyte, which solves the previous problems observed using BiFE systems.

2. Experimental

2.1. Reagents and solutions

Stock solutions of thiol (*n*-dodecyl mercaptan, *n*-C₁₂H₂₅SH) was prepared by diluting the samples in *n*-octane (*n*-C₈H₁₈) giving a concentration of 10 mg mL⁻¹, and standard solutions were made daily by appropriate dilution of the stock solution [32]. A methanol solution containing 1.4 mol L⁻¹ sodium acetate and 0.35 mol L⁻¹ acetic acid was taken as the supporting electrolyte, which provided enough electronic conductivity and intermiscibility after the addition of small volume of *n*-octane [18,33]. The Bi stock solutions with different concentrations (5.0 × 10⁻² mol L⁻¹, 1.0 × 10⁻² mol L⁻¹, 5.0 × 10⁻³ mol L⁻¹) were prepared by dissolving bismuth nitrate (Bi(NO₃)₃·5H₂O) in 10% HNO₃ solution. All chemicals were analytical-grade reagents and obtained from Beijing Chemical Technology Company (Beijing, China).

2.2. Electrochemical analysis method

All electrochemical measurements were performed with an electrochemistry workstation (PARSTAT 2273). The temperature

in these experiments was kept at 40 °C for better diffusion of fuel but was limited by the boiling point of methanol in the electrolyte. A three electrodes system was used with a glass carbon electrode (GCE, *d* = 3 mm) as a substrate for forming *in situ* BiFE, a platinum plate as the auxiliary electrode and an Ag/Ag⁺ as the reference electrode. To guarantee the precision of reference electrode, double pipe was adopted by adding standard solution of Ag/Ag⁺ (0.1 mol L⁻¹ AgNO₃ dissolved in acetonitrile) in internal pipe and methanol electrolyte in external pipe. The GCE was cleaned carefully before utilization, as described in previous work [34].

45.0 mL of the supporting electrolyte and 5.0 mL of the bismuth stock solution were added into the electrochemical cell, and then the *in situ* Bi film could be formed on substrate of GCE when the potential was negative than -0.8 V. In order to ensure the intermiscibility and conductivity of the electrolyte, the volume ratio of sample to the supporting electrolyte was kept about 1:10,000. For example, 5.0 μL of fuel sample was added into 50.0 mL of the supporting electrolyte. After the sample and the bismuth stock solution were added into the electrolyte, it was stirred for 10 s and then equilibrated for 10 s. Afterward the potential was negatively scanned from -0.7 V to -1.3 V, and then positively scanned to 0.4 V, and finally ended at -0.7 V with the scan rate of 50 mV s⁻¹. After each measurement, the electrode was cleaned by applying -0.2 V for 50 s under stirring in order to remove all deposited material from GCE. All of the measurements were carried out in deaerated electrolyte and argon blanket was kept above the electrolyte during the measurement.

3. Results and discussion

3.1. The CV curves in the electrolyte containing Bi^{III}

The acetic acid-sodium acetate/methanol solution is a typical non-aqueous electrolyte [18], in which the acetic acid-sodium acetate buffer provides considerable electro-conductivity. Methanol does not display any electrochemical behavior below its oxidation potential of 1.04 V [33] and is only able to dissolve a small amount of nonpolar fuel. The blank CV curve of GCE is shown in Fig. 1a. The broad peak near -1.2 V may be the result of the reduction of acetic acid in the electrolyte [35]. A remarkable pair of cathodic and anodic peaks appear in the range of -1.0 V to -0.5 V when Bi^{III} ions were present in the supporting electrolyte (Fig. 1b). These peaks correspond to the formation and elimination of the Bi film on the surface of GCE. The cathodic peak near -0.90 V was results from the reduction of Bi^{III} to Bi, forming the Bi film on GCE. After scanning over positive potentials, the Bi film dissolves (oxidizing Bi to form Bi^{III}) and an anodic peak is observed at -0.60 V. The potential difference of 0.30 V between the anodic and cathodic peaks is similar to that in the aqueous electrolyte (-0.26 V and -0.66 V) [29], indicating the reversibility of the Bi^{III}/Bi pair in the methanol electrolyte. It is important to note that the current intensity in the range of -0.7 V to -0.9 V was different for the positive and negative scanning directions, indicating that there was about 30 μA of cathodic current remaining during the positive potential scan (Fig. 1b). This result could be explained by the continual deposition of Bi^{III} ions on the electrode after the first layer of Bi film is formed on GCE.

3.2. The CV curves in the electrolyte containing Bi^{III} and thiol

If *n*-C₁₂H₂₅SH is added to the methanol electrolyte without any Bi^{III} ions present, the CV curves appear the same as the blank one (Fig. 2a), indicating that the thiol molecules themselves have no electrochemical reaction on GCE. When both of *n*-C₁₂H₂₅SH and Bi^{III} are present in the electrolyte, the cathodic and anodic peaks

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