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Review article

Determination of sulfur compounds in gasoline using mercury film electrode by square wave voltammetry

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Abstract

A sensitive method based on square wave voltammetry is described for the quantitative determination of elemental sulfur, disulfide and mercaptan in gasoline using a mercury film electrode. These sulfur compounds can be quantified by direct dissolution of gasoline in a supporting electrolyte followed by subsequent voltammetric measurement. The supporting electrolyte is 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol. Chemical and optimum operational conditions for the formation of the mercury film were analyzed in this study. The values obtained were a 4.3 μm thickness for the mercury film, a 1000 rpm rotation frequency, −0.9 V applied potential and 600 s depositing time. Voltammetric measurements were obtained using square wave voltammetry with detection limits of the 3.0×10^{-9}, 1.6×10^{-7} and 4.9×10^{-7} mol L^{-1} for elemental sulfur, disulfide and mercaptan, respectively.

Keywords: Sulfur compounds; Square wave voltammetry; Mercury film electrode; Gasoline

Contents

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1. Introduction

Due to the importance of sulfur in chemical, biological and industrial areas, sulfur compounds have been extensively studied for many years [1–5], especially the determination of sulfur and its compounds in drugs, cosmetics, foodstuff, and petroleum products [6–9].

Sulfur has been the most abundant element in petroleum after carbon and hydrogen for many years [10]. Nowadays, in the case of the products resulting from the degradation of organisms, oxygen and nitrogen are more abundant than sulfur. It has been demonstrated that sulfur penetrates into organic matter before crude oil is extracted and also after the sedimentation process [11]. For a long period, reducing bacteria in sediments have made changes in sulfate salts and have altered the formation of sulfur reducing compounds such as H_2S, S^0, sulfite, mercaptan and polysulfide. In other words, these sulfur species are produced by anaerobic bacterial reduction of sedimentary sulfate deposits (mainly anhydrite or gypsum). The anaerobic bacteria consume sulfur instead of O_2 as a source of energy and a hydrogen acceptor to produce these sulfur compounds [12]. Apparently the reactions of these sulfur species and the formation of C–S bonds cause the occurrence of organosulfur compounds in petroleum derivatives. In order to properly remove sulfur from petroleum and its derivatives, such as LPG, naphtha, gasoline, kerosene, gas oil and lubricants, it is necessary to appropriately design oil facilities and develop a methodology to determine sulfur compounds especially in quality-control units.

Because various metals can suffer the corrosive effect of the sulfur compounds remaining after the refining of petroleum, it is interesting to have analytical methods to detect and determine the most common sulfur compounds in the refining industry. Several methods for the determination of sulfur compounds have been reported, including colorimetric [13], titration [14], chromatographic [15], iodimetric [16,17] and X-ray fluorescence spectrometry [18,19]. These methods are accurate and sensitive for the determination of elemental sulfur and mercaptan, but they are time-consuming and tedious. In contrast to these methods, electrochemical procedures are highly promising for obtaining high sensitivity at good speed, low cost and a low detection limit.

The general application of the electrochemical methods for the analysis of sulfur compounds include polarography to determine inorganic and organic compounds in petrochemical analysis [20–22]. Usually, the polarographic methods have been applied to the determination of only one kind of sulfur compound, using solvents such as methanol and pyridine. Some works targeting the determination of total sulfur, hydrogen sulfide, elemental sulfur [23], organic sulfur compounds and elemental sulfur [24] in oil fractions have been reported. On the other hand, elemental sulfur in fuels [25] and mercaptan sulfur in synthetic samples [26] have been determined using differential pulse polarography.

Kashiki and Ishida [27] accomplished the study of the determination of mercaptan, disulfide and elemental sulfur in petroleum naphtha using square-wave polarography implementing a dropping mercury electrode.

Chemically modified electrode also have been used for determination of sulfur compounds in pharmaceutical formulations using boron doped diamond electrode [28], determination of sulfite in sugar using aluminum electrode modified by nickel pentacyanonitrosylferrate film [29] as well as the analysis of sulfide in cigarette smoke using chemically modified screen-printed electrode [30].

An important drawback to electroanalytical techniques is often attributed to the frequent necessity of using a hanging mercury drop electrode (HMDE), but its use has been limited to analytical procedures due to the hazardous effects of mercury. However, some molecules such as those of the sulfur-compound class for example are electroactive on a mercury surface, thus requiring the use of mercury and the consequent risk of contamination. Having the main objective of a avoiding the use of mercury in such analysis, several modifications of electrode surfaces have been proposed. Due to this problem, allied to the highly toxic nature of mercury, the research for new simple electrochemical electrodes for analysis and study of sulfur compounds in fuel as well as other organic and inorganic compounds is necessary. In this context, the mercury film deposited on a glassy-carbon electrode is a convenient electrode surface because it is practically non-toxic, easily prepared and is simple to regenerate electrochemically or manually.

Chemical modification of electrode surfaces to carry out mechanical or electrochemical analysis has several advantages in terms of selectivity, sensitivity and efficiency for the determination of a species using electroanalytical techniques [31–33], including metal analysis of petroleum derived from fossil fuels [34,35].

In this context, a successful electrode for analysis is a mercury-film electrode (MFE) comprising a thin layer of mercury salt electrodeposited on a conventional solid and an inert surface such as glassy carbon. This kind of electrode has experimental advantages such as high surface area/volume ratio, resulting in a higher concentration of amalgam during the deposition step, which increases the sensitivity. Additionally, MFE has a high mechanical resistance, being stable under vigorously stirring or coupled with flow systems [36–38]. This feature increases their applicability.

Several works have been reported in the literature using the mercury-film electrode, among them are works which undertake the determination of pollutants such as the pesticide atrazine in soil and water [39] and the determination of sulfite in food using a sulfite-oxidase biosensor-based glassy-carbon electrode coated with a thin mercury film [40] as well as the simultaneous determination of zinc, copper, lead and cadmium in fuel ethanol [41].

Despite the importance of quality control for sulfur compounds in fuel, the literature contains no reports of