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ORIGINAL PAPER

Electrochemical determination of elemental sulfur in Brazilian naphtha: method and validation

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Abstract Sulfur compounds in petroleum have caused several problems such as corrosion of equipment, lack of high quality final products, and emission of toxic gases into the environment. Elemental sulfur can increase these problems, since small amounts of it turn mercaptans into potential corrosion agents. This paper describes the applicability of a voltammetric method to quantify elemental sulfur in Brazilian naphtha samples. Elemental sulfur was quantified in synthetic and real samples using square wave voltammetry and a hanging mercury drop electrode. The method was found to have low limits of detection (0.003 mg L^{-1}) and quantification (0.009 mg L^{-1}) and a good recovery range (94.0–108.6%). This voltammetric method has potential for use in elemental sulfur determination in naphtha samples containing mercaptans and aliphatic and aromatic disulfides.

Keywords Elemental sulfur · Voltammetry · Naphtha-validation

1 Introduction

Due to the importance of sulfur in chemical, biological and industrial areas, sulfur compounds have been studied intensively for many years [1–5], especially with regard to the determination of sulfur and its compounds in drugs and natural and petroleum products. Sulfur is found in petroleum in several forms. In light fractions, the sulfur species are elemental sulfur, sulfidric acid, mercaptans and disulfides, with the acid mercaptan forms dominating. In heavy fractions, compounds such as thiophene and its derivatives are the most abundant [6]. The complexity of these sulfur compound mixtures depends not only on the origin of the petroleum but also on the refining process. Some of the compounds (such as elemental sulfur), either alone or in combination, have been associated with undesirable characteristics in the final products [7].

The determination of elemental sulfur in naphtha samples is of great interest because it is known that sulfur causes, not only corrosion of equipment, but also damage to catalysts, decreasing the quality of the final product. It can also impair the efficiency of lubricants and antioxidants. Elemental sulfur, even in low concentrations (less than 1 ppm), deserves special attention because it is capable of catalyzing the formation of other sulfur species in petroleum, such as sulfides, disulfides, polysulfides, and mercaptans, significantly changing their concentrations [7, 8]. In addition, in the presence of mercaptans, elemental sulfur has a synergistic corrosive effect [9, 10]. Another equally important issue is the emission of toxic gases into the environment; these must be minimized according to environmental legislation.

For all these reasons, it is important and necessary for the petroleum industry to improve methods used to determine the elemental sulfur content, specifically by proposing a faster and more efficient analysis.

The allowed limit for total sulfur in Brazilian naphtha samples is 500 ppm. It is known that sulfidric acid, elemental sulfur, mercaptans and disulfides correspond to

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approximately 1% of the total sulfur content in napthas. Therefore, methods for determining trace amounts of elemental sulfur have been a great challenge in the area of chemical analysis. The large number of analytical methods that have been proposed for determination of elemental sulfur indicates that there is no established quantitative method for the direct determination of trace quantities of elemental sulfur in petroleum matrices [11–16]. In fact, the most common methods found in the literature were developed to quantify total sulfur [5] and sulfide [1, 8] compounds.

Voltammetric techniques show interesting characteristics, such as establishing direct relationships between the analyte concentration and electrical properties such as current, potential, conductivity, resistance, and charge. An advantage of this technique is the ability to analyze samples directly, without previous purification and separation. In addition, analysis of colored materials or samples containing dispersed solid particles is possible. These advantages, along with the possibility of in situ analysis, a short analysis time, and lower cost of instrumentation and materials, when compared with chromatographic and spectroscopic techniques, make it an extensively used technique [17]. Voltammetry in the petroleum industry was initially used in the analysis of sulfur and its compounds, naphthalene and its derivatives, hydroperoxides, antioxidants and trace metals [17].

Table 1 shows some voltammetric applications for elemental sulfur determination in petroleum and its derivatives [18–28]. Elemental sulfur has been studied for many decades [17], and few changes have been observed from one methodology to another. Different working mercury electrodes, electrolyte solutions and techniques have been combined to achieve better analytical conditions, as well as faster and more accurate analysis.

These studies highlight several difficulties in analyzing elemental sulfur in petroleum samples and their derivatives. The complexity of the matrix and the presence of interferents show the importance of studying, developing, and validating increasingly more precise, sensitive, and faster methods to satisfy the quality needs of the petroleum industry.

In this paper, we describe a very sensitive and quick procedure for the determination of elemental sulfur where a small amount of sample is directly analyzed in an electrochemical cell using a hanging mercury drop electrode.

2 Experimental section

2.1 Chemicals, apparatus and procedure

All reagents were of pure grade and were used without further purification, except for metallic copper powder,

Table 1 Voltammetric application for elemental sulfur determinations

Technique[a]	Electrode[b]	Electrolyte[c]	Samples[d]	DL ($mg\ L^{-1}$)	Precision	Accuracy (%)	Work range ($mg\ L^{-1}$)	Reference
A.C.	DME	CH_3OH/Pir./HCl	Gasoline	1	–	2	1–100	[18]
A.C.	DME	CH_3OH/Bnz./$H_3CCOONH_4$/H_3CCOOH	Petroleum derivatives	–	1%	<5	4–40	[19]
A.C.	DME	CH_3OH/Pir./HCl	LPG	0.01	2%	>2	0.02–4.3	[20]
SWV	DME	CH_3OH/$H_3CCOONa$/H_3CCOOH	Naphthas	0.5	–	6	0.5–30	[21]
SWV	DME	CH_3OH/$H_3CCOONa$/H_3CCOOH/CH_3I	LPG	0.01	–	4.8	0.001–0.100	[22]
–	DME	CH_3OH/Bnz./H_2O/acetate buffer	Gasoline	0.003	–	>20	1–10	[23]
A.C.	DME	CH_3OH/LiCl/Pir./HCl	Petroleum/LPG	0.1	–	–	–	[24]
DPV	HMDE	CH_3OH/Tol./$H_3CCOONH_4$/H_3CCOOH	Fuel	0.1	<10% to 1 $mg\ L^{-1}$	<5	2–30	[25]
A.C.	HMDE	CH_3OH/Tol./NaCl/NaOH	Electrolyte	0.016	–	–	0.03–2560	[26]
DPV	DME	H_2SO_4/Tol./Ethanol	Petroleum derivatives	0,0001	3.3% to 0.001 $mg\ L^{-1}$	<5	0.0002–0.035	[27]
SWV	MFE	CH_3OH/$H_3CCOONa$/H_3CCOOH	Gasoline	0.0008	0.5% to 2.6 $mg\ L^{-1}$	–	2.56–20	[28]

[a] *A.C.* alternating current, *SWV* square wave voltammetry, *DPV* differential pulse voltammetry

[b] *DME* dropping mercury electrode, *HMDE* hanging mercury drop electrode, *MFE* mercury film electrode

[c] *Pir.* pyridine, *Tol.* toluene, *Bnz.* benzene

[d] *LPG* liquefied petroleum gas

which was passed through an activation process. Methanol, ethanol, acetone, diethyl ether, 70 wt% nitric acid, 99 wt% glacial acetic acid, sodium acetate, *n*-heptane, 1-butanethyol, 1-propanethyol, 2-methyl-2-propanethyol, dipropyl disulfide, diphenyl disulfide, elemental sulfur monoclinic, and metallic copper powder (particles <63 µm and >230 mesh) were purchased from Merck. All sulfur standards were stored at temperatures between 10 and 15 °C.

The electrochemical cell was composed of a HMDE (hanging mercury drop electrode) as the working electrode, $Ag/AgCl/Cl^-$ as the reference electrode, and platinum wire as the auxiliary electrode. The supporting electrolyte was a buffer solution containing 2% (v/v) glacial acetic acid and 1.4 mol L^{-1} sodium acetate in methanol.

The voltammetric analysis was performed using a Radiometer potentiostat (Voltalab 80) using square wave voltammetry (SWV).

For the voltammetric analysis procedure, 10 mL of the supporting electrolyte solution was pipetted into the electrochemical cell and purged with nitrogen for 300 s to eliminate oxygen. Aliquots of real naphtha samples (300 µL) were analyzed in triplicate in the presence of the supporting electrolyte after purging with nitrogen for an additional 300 s. Some specific parameters used in all analyses were a 50 µm capillary size, 3.8 s drop-growing time, 500 rpm stirring rate, 15 mV potential step, 50 mV pulse amplitude, 1 s pulse time, 1 s potential step time, 0.5 bar pressure, 300 mV s^{-1} scan rate and potential range from −0.100 to −0.800 V. All parameters were optimized in this work and differ significantly from previously reported determinations [21]. A calibration curve was constructed before each set of analyses. This was done by plotting peak area versus elemental sulfur concentration. All the graphics in this paper were obtained under these conditions.

2.2 Quantification of elemental sulfur

We performed a recovery study with synthetic samples employing the proposed voltammetric method, subsequently applying this study to eight real naphtha samples. The quantification of elemental sulfur was calculated as shown in the following equation:

$$S(\mathrm{mg\,L^{-1}}) = \frac{(V_e + V_s)}{V_s} C(\mathrm{mg\,L^{-1}}) \qquad (1)$$

where S is the elemental sulfur concentration in the sample, V_e is the volume (mL) of the solution, V_s is the volume (mL) of the synthetic sample, and C is the concentration obtained from the calibration curve.

The copper strip tarnish test was carried out in all real naphtha samples according to the ASTM D130 method [29]. This test was used as a reference for all real naphtha samples studied.

2.3 Copper column and its activation procedure

A copper column was used for each sample to eliminate the interference of disulfides in voltammetric analyses [21]. The optimized parameters were: column diameter (0.5 cm), column height (18.0 cm), mass of copper (2.0 g), naphtha sample volume (2.0 mL) and flow of naphtha sample in the column (atmospheric pressure). Optimization was performed using a mixture containing 2 mg L^{-1} of elemental sulfur, 10^2 mg L^{-1} of 1-butanethyol, and 10^3 mg L^{-1} of dipropyl disulfide. It was necessary to activate the copper before using the column. To do so, the copper was successively washed with 10% (v/v) nitric acid, distilled water, ethanol, acetone and diethyl ether. In addition, the copper was filtered and dried in a vacuum desiccator. The anhydrous copper was used immediately after weighing and preparing the column to avoid oxygen adsorption.

The amount of elemental sulfur can be calculated by subtracting the area of the peak relative to the voltammetric curve after passing the sample through a copper column (due to the presence of disulfide) from the total peak of the real naphtha sample (which is obtained before passing the sample through a copper column).

3 Validation study

Validation of the voltammetric method for quantitative determination of elemental sulfur in naphtha samples was performed via several steps, which were important to ensure the reliability of the obtained results [30, 31].

3.1 Selectivity and linearity

The selectivity of the method was evaluated through the separate analyses of 300 µL each of benzene, toluene, olefins, disulfides, mercaptans, and thiophene and its derivatives (possible interferents) in an electrochemical cell with 10 mL of electrolyte solution. The analysis was performed at the aforementioned conditions used for this method.

The linearity study was done using standard elemental sulfur solutions that were analyzed in five concentrations ranging from 0.010 mg L^{-1} to 0.238 mg L^{-1}. The analysis was performed in triplicate for each concentration (Table 2).

3.2 Detection and quantification limits

The detection and quantification limits were determined, respectively, according to 3σ and 10σ criteria of the blank measurements [30, 31]. The blank sample was a mixture of the supporting electrolyte and solvent. For this, five electrochemical cells containing the blank solutions were analyzed, and the analysis was performed in triplicate for each cell (Table 3). The Grubbs test was applied with 95% confidence toward elimination of outliers [31]. After applying the Cochran test for each set of variance values, it was concluded that the variances were statistically equivalent and could therefore be grouped. Thus, a final medium blank value was obtained for determination of the limits of detection and quantification. The equations used were:

$$\mathrm{DL} = 3\sigma + \overline{Y_\mathrm{B}} \tag{2}$$

$$\mathrm{QL} = 10\sigma + \overline{Y_\mathrm{B}} \tag{3}$$

where DL is the detection limit, QL is the quantification limit, σ is the standard deviation from the analysis of the blank samples, and $\overline{Y_\mathrm{B}}$ is the mean value of all analyses of blank samples.

The detection and quantification limits were also determined experimentally. Different concentrations of elemental sulfur (0.005, 0.004, 0.003, 0.002 and 0.001 mg L^{-1}) were separately analyzed in an electrochemical cell in the order of decreasing elemental sulfur concentration until no signal was observed in the voltammogram. The experimental detection limit was obtained from the elemental sulfur current signal, which was at least three times the magnitude of the largest noise in the voltammogram.

3.3 Recovery

Standard solutions of elemental sulfur were prepared. Several aliquots were added into the electrolyte cell with 10 mL of electrolyte solution. These aliquots were added according to the established concentrations, which were 0.015, 0.025, 0.035, 0.044, 0.058, 0.116, 0.175 and 0.233 mg L^{-1} (Table 4).

3.4 Precision, accuracy and robustness

Two operators (A and B) devised the procedure for constructing the two calibration curves. The results were obtained for 0.010, 0.030, 0.050, 0.146 and 0.238 mg L^{-1} of elemental sulfur in *n*-heptane.

Precision was evaluated by repeatability and the intermediate precisions of the analyses. The repeatability was analyzed from the results obtained on the same day for operator A whereas the intermediate precision was evaluated by comparison of the results of the two operators (A and B) on different days on the same instrument (Tables 2 and 5).

The robustness of a method evaluates its sensitivity to small changes. This was verified through repeatability and intermediate precision studies. Accuracy was evaluated using the results of the recovery study.

3.5 Study of the variances and residue analysis

The results of any quantitative method that can be described by a linear regression model should present calibration curves with significantly constant (homogenous) variances. This is called homoscedasticity. When these variances increase together with the concentration of the analyzed species, the homoscedastic condition is violated (heteroscedasticity). To evaluate if the applied method is homo- or heteroscedastic, the Cochran test was used. This test estimates the bilateral deviation of the variances at a significance level of 5%. The unique limitation for its use is the replication number, which should be equal for all measured series [30].

The residue is represented by the difference between the measured value and that predicted by the model. The residue analysis was evaluated in order to assure both the regression model and the variances behavior [30]. A residual plot was prepared for each set of analysis (Fig. 5).

3.6 Comparison between two different calibration curves

To evaluate the slope of the two calibration curves, which were obtained from distinct operators, a sequence of statistical calculations was necessary. First, the residual variance (Se^2) was determined for each calibration curve [30, 31]. Then, the Snedecor test was applied to verify if the residual variances were significantly different [30, 31]. When the calculated F value (F_cal) is lower than the critical F value (F_crit), the variances can be considered statistically equivalent. In the second step, the grouped variance (S^2_ep) was calculated for each calibration curve (A and B operators).

In the last step, the calculated t value (t_cal) was obtained [30, 31] and compared with the critical t value (t_crit) to six degrees of freedom for a 5% significance level. If t_cal is lower than t_crit, then the slopes of the two calibration curves can be considered statistically equivalent (Table 6).

4 Results and discussion

4.1 Electroactivity

The electroactivity of elemental sulfur was investigated. It was observed that elemental sulfur was electroactive in the potential range −0.500 to −0.670 V. Figure 1, which shows an example of this behavior, contains the voltammograms taken of elemental sulfur dissolved in *n*-heptane.

In this potential range, two electrons are involved in the electrode reaction and the reduction of elemental sulfur occurs according to the following equation [18]:

$$S + 2H^{+} + 2e^{-} \rightarrow H_2S \qquad (4)$$

It was observed that the elemental sulfur concentration was proportional to the area of the peak on the voltammogram.

4.2 Selectivity

Figure 2 shows the electrochemical behavior of the sulfur-containing species. Two mercaptans were evaluated: 2-methyl-2-propanethyol and 1-propanethyol. The behavior was comparable for both mercaptans which were electroactive in a different potential range than elemental sulfur, namely, between −0.300 and −0.500 V. Therefore, they did not interfere in these analyses. To evaluate the electroactivity of disulfides, we studied aliphatic (dipropyl-disulfide) and aromatic (diphenyl-disulfide) species. Aliphatic disulfides were electroactive in the same potential range of the elemental sulfur, from −0.500 to −0.670 V but they may interfere only when the concentration is equal to or greater than 6500 mg L^{-1}, which is improbable in naphtha. Although aromatic disulfides do not frequently occur in naphtha samples, they may interfere when their concentration is higher than 5 mg L^{-1} in the analyses.

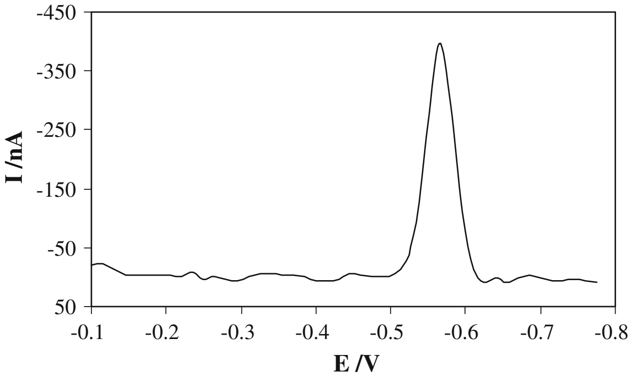

Fig. 1 Square wave voltammogram of elemental sulfur in 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol

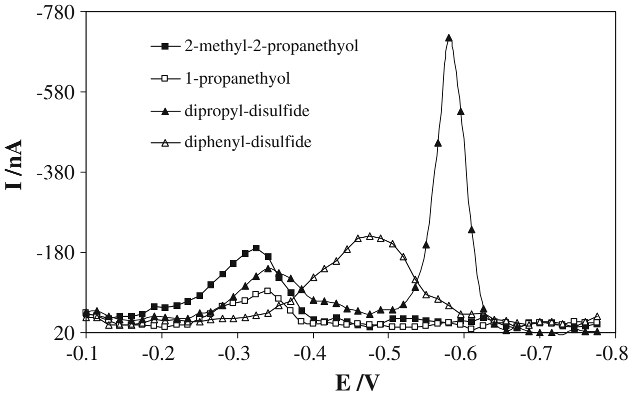

Fig. 2 Square wave voltammograms of mercaptans and disulfides in 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol

Other possible interferents present in Brazilian naphtha, such as benzene, toluene, olefins, and thiophene and its derivatives, were inactive in the elemental sulfur potential range.

4.3 Elimination of interferences

A copper powder column was chosen to eliminate the interferents in this analysis. Figure 3 shows the application of this column in a real naphtha sample. When the analysis was performed without passing the sample through a copper column, elemental sulfur, disulfides and mercaptans could be seen in their electroactivity ranges. After passing the sample through the copper column, elemental sulfur and mercaptans disappear, probably because they react with copper, forming cuprous mercaptide, whereas disulfides do not react. To guarantee that all elemental sulfur and mercaptans react with the copper, it is necessary to use at least one column of copper for each real naphtha sample. However, if mercaptans are to remain in the analysis after passing the copper column, the analysis must be repeated by passing the real naphtha sample twice through the copper column.

4.4 Linearity

Table 2 shows the data for two calibration curves, their variance and RSD values for different standard concentrations of elemental sulfur in solution. For both curves, the Cochran test was applied, and the results ($C_{\text{calc}} < C_{\text{crit}}$) show that the data are homoscedastic in the range studied, meaning that linear regression could be used.

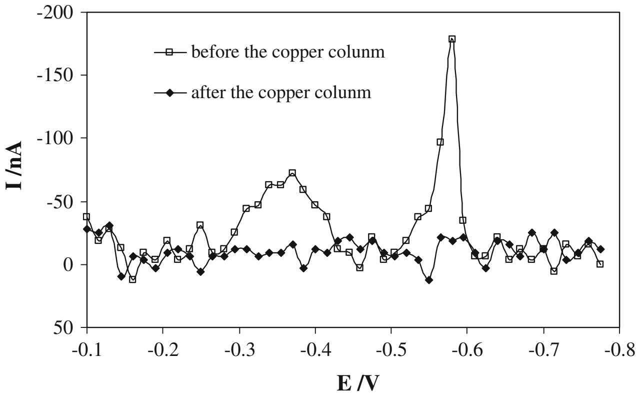

Fig. 3 Square wave voltammogram of the Brazilian naphtha sample in 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol

To continue evaluation of the method's linearity, the second curve was used because the correlation coefficients were not significantly different ($R_1 = 0.9982$ and $R_2 = 0.9975$). The value of R higher than 99.8% is considered acceptable for this kind of analysis. Figure 4 shows the relationship between a given area value (in nW) and the concentration (in mg L^{-1}) corresponding to that area. According to the residual plot, the residues are aleatorically distributed around the zero line (straight line) and that no pattern is observed. This means that the proposed linear model is adequate to describe the data distribution (Fig. 5).

4.5 Limits of detection and quantification

Table 3 shows some of the results used for calculation of the detection and quantification limits based on Eqs. 2 and 3, respectively [30, 31]. No value was rejected by the Grubbs test. When the Cochran test was applied, the variance values were not significantly different ($C_{\text{calc}} < C_{\text{crit}}$). The mean values and standard deviation of all analyses of blank samples were used to calculate the detection and quantification limits. They were, respectively, 0.001 and 0.008 mg L^{-1}.

Quantification and detection limits determined by both statistic and experimental methodologies show a difference smaller than the standard deviation verified for the blank samples. The value in Table 4 expressing the standard deviation, when converted to concentration, represents approximately 0.004 mg L^{-1} of concentration. Therefore, these quantification (0.008 and 0.009 mg L^{-1}) and detection (0.001 and 0.003 mg L^{-1}) values can be seen as comparable. However, to guarantee a good safety margin for the method application, it might be a good choice to select DL and QL as 0.003 and 0.009 mg L^{-1}, respectively.

Table 2 Validation study of synthetic samples using elemental sulfur (operator A)

S concentration (mg L^{-1})	0.010	0.030	0.050	0.146	0.238
Area average (nW)	23.825	73.143	124.49	290.80	451.93
S^2	1.239	16.790	5.8820	7.3750	29.342
RSD	4.67	5.60	1.95	0.93	1.20
C_{cal}	0.483				
Area average (nW)	23.785	74.221	121.89	276.77	479.19
S^2	0.9820	1.789	35.428	4.156	59.787
RSD	4.16	1.80	4.88	0.74	1.61
C_{cal}	0.585				
C_{crit}	0.684				

All values of area were considered with 95% of confidence, S^2 variance, *DRS* relative standard deviation, C_{cal} calculated value of Cochran and C_{crit} critical value of Cochran

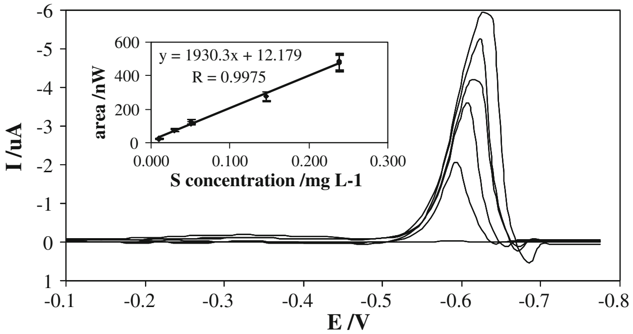

Fig. 4 Calibration curve of elemental sulfur constructed from all values of a standard solution of elemental sulfur in 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol

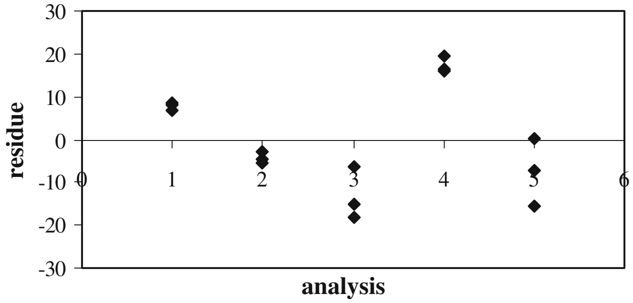

Fig. 5 Graphic of the residue analysis constructed from all values of a standard solution of elemental sulfur in 1.4 mol L^{-1} sodium acetate and 2% acetic acid in methanol

Table 3 Blank data used for the determination of detection and quantification limits of voltammetric method

Cell	Area average (nW)	S^2	*S*
1	3.6389	5.8299	2.4145
2	3.0412	4.2233	2.0551
3	4.6366	7.3618	2.7133
4	3.4633	8.7586	2.9594
5	2.7859	1.7086	1.0385
Average	3.5131	5.5764	2.3614
$C_{\text{cal}} = 0.314$		$C_{\text{crit}} = 0.684$	

S^2 variance, *S* standard deviation, C_{calc} calculated Cochran value; C_{crit} critical Cochran value with 95% of confidence

According to Table 1, Kashiki et al. reported a methodology for quantifying elemental sulfur in naphtha samples using the same technique and working electrode employed in the proposed method [21]. The detection limit was found to be 0.5 mg L^{-1}. Therefore, the proposed method has a detection limit smaller than that used by Kashik et al. However, works by Sid Kalal et al. [27] and Serafim and Stradiotto [28] reported detections limits of 0.0001 mg L^{-1} and 0.0008 mg L^{-1}, respectively, which are lower than that obtained by the proposed method.

Although their studies employ different techniques and working electrodes, their methodologies were those that reported the smallest DL up to now.

4.6 Recovery study

Table 4 shows the recovery results obtained from synthetic samples of different concentrations of elemental sulfur. The voltammetric method presented recovery values between 94.0 and 108.6% and a relative error lower than 10%. These results suggest a good performance, considering the trace recovery elemental sulfur concentrations.

4.7 Precision

Considering the data for each operator separately, good repeatability was verified; e.g., there were only small variations in the results of the triplicate analyses performed within a short time using the same conditions. The relative standard deviation values for operator A were lower than 6%, while those of operator B were lower than 9% (Tables 2 and 5). For this kind of technique, this is considered acceptable.

A comparison has also been done between the calibration curves performed by the two different operators employing the same proposed method using the same voltammetric analyzer. Tables 2 and 5 present the obtained results by operators A and B, respectively. Table 6 shows that there is no significant difference between the calibration curves from the two operators.

Olofsson reported a determination of elemental sulfur in Jet Fuel by DPV using a static mercury drop electrode. The amount of 1 mL of a real sample was directly added into 9 mL of electrolyte solution consisting of 0.19 mol L^{-1} ammonium acetate and acetic acid in 1:1 (v/v) methanol and toluene [25]. The method presented a precision of less than 10% for 1 mg L^{-1} of elemental sulfur. A disadvantage of this method is the use of toxic solvents such as ammonium and toluene. Sid Kalal et al. [27] reported the determination of trace elemental sulfur in petroleum and its distillates by DPV detection using a dropping mercury electrode. However, a preliminary extraction of the real sample (an amount of 50–200 mL) is necessary, making the method more extensive than others. A precision of 3.3% was found for 0.001 mg L^{-1} of elemental sulfur concentration ($n = 4$). Serafim and Stradiotto [28] reported a determination of elemental sulfur in gasoline using a mercury film electrode by square wave voltammetry. Each 1 mL gasoline sample was added to 10 mL of the solution of sodium acetate and acetic acid in methanol (electrolyte solution). A precision of 0.5% was verified from the repeatability of 10 determinations of 2.6 mg L^{-1} for elemental sulfur. In this methodology, an additional step of the working electrode preparation is introduced, rendering the analysis still more extensive.

Table 4 Results from the recovery study, determined by the voltammetric method on synthetic samples of elemental sulfur

Sample	$S_{content}$ (mg L^{-1})	S_{found} (mg L^{-1})	Recovery (%)	Error (%)
1	0.015	0.016	106.7	6.6
2	0.025	0.024	96.0	4.0
3	0.035	0.038	108.6	8.6
4	0.044	0.043	97.7	2.3
5	0.058	0.059	101.7	1.7
6	0.116	0.109	94.0	6.0
7	0.175	0.181	103.4	3.4
8	0.233	0.250	107.3	7.3

Table 5 Validation of synthetic samples containing elemental sulfur (operator B)

S concentration (mg L^{-1})	0.010	0.030	0.050	0.146	0.238
Area average (nW)	15.311	64.527	96.317	283.93	465.99
S^2	0.9830	0.8170	26.503	50.052	80.521
RSD	6.47	1.40	5.34	2.49	1.92
C_{cal}	0.507				
Area average (nW)	16.284	61.803	95.649	267.53	436.97
S^2	21.838	27.079	4.106	14.895	42.721
RSD	2.87	8.41	2.12	1.44	1.49
C_{cal}	0.386				
C_{crit}	0.684				

All values of area were considered with 95% of confidence, S^2 variance, *DRS* relative standard deviation, C_{cal} calculated value of Cochran and C_{crit} critical value of Cochran

Table 6 Sources of variance: results of analyses performed by different operators

Operator	n	Linear regression equation	R	Se^2
A	5	(area) = 1883.6 (S concentration) +15.244	0.9987	110.4
B	5	(area) = 1897.7 (S concentration) + 0.09	0.9993	59.63
$F_{cal} = 1.85$		$F_{crit} = 9.605$		

R coefficient of variation, *n* number of points of curve, Se^2 residual variance, F_{calc} calculated Snedecor *F* value and F_{crit} critical Snedecor *F* value

The precision of the proposed method was obtained for a different work range those reported in the literature. Therefore, it can not be comparable. However, the proposed method presents a good precision considering the kind of analysis employed. Moreover, the proposed method presents advantages such as a precise and faster analysis, a small amount of sample (0.3 mL) added directly to the electrochemical cell (without previous purification and separation), needs no preliminary preparation of the working electrode and uses solvents that are less toxic than ammonium and toluene.

4.8 Real naphtha sample analyses

To evaluate the applicability of the voltammetric method to real naphtha eight samples were analyzed in triplicate. Table 7 shows the medium values of concentration for each sample with their confidence intervals, which were calculated by the equation $t\sigma/\sqrt{n}$ (t is the t-Student value, σ is the standard deviation, and n is the number of sample replications). The concentrations of elemental sulfur were found to be lower than 2 mg L^{-1}. The qualitative copper strip test was carried out in all samples, and its results are shown in Table 7. According to this test, naphtha samples with up to 5 ppm of elemental sulfur present classification of 1 and 2, whereas samples with more than 6 ppm present classification 3 and 4. Some real naphtha samples produce a deposit over the copper strip and cannot be evaluated by the copper test, because this deposit can distort the results. However, the real naphtha samples 1, 3, 4 and 6 present elemental sulfur concentrations lower than 5 mg L^{-1} and classification 1 and 2 according to the copper test. Therefore, the concentration of elemental sulfur content in naphtha samples was in agreement with the copper strip test.

5 Conclusions

The voltammetric method presented is of interest for the determination of elemental sulfur in naphtha samples. In the concentration range studied, the response is linear. This concentration range permits quantification of elemental sulfur in very low concentrations. The detection and quantification limits were considered good for this kind of analysis. The method showed good recovery, precision and accuracy. Therefore, the voltammetric method can be proposed to quantify elemental sulfur in naphtha samples.

Comparison of the method with those reported in the literature shows that this one allows for faster analysis, use of less toxic solvents when compared to pyridine and toluene, use of fewer reagents, addition of samples directly to the analysis cells, and finally, a lower cost for instrumentation and maintenance. Although mercury is toxic, the quantity used in these analyses is very low. Moreover, the HMDE electrode is more practical than other electrodes because it can be commercialized and the mercury can be reused. Therefore, it is a good choice of electrode for elemental sulfur analysis in the petroleum industry.

The use of a methodology to quantify elemental sulfur in the petroleum industry results in better quality control of the final products from a refinery, thus ameliorating several environmental and industrial problems.

Table 7 Results obtained from real naphtha samples

Sample	S_{found} (mg L^{-1})	Copper strip tarnish test
1	1.3643 ± 0.1410	1a
2	0.9581 ± 0.1869	*
3	1.8676 ± 0.1407	2b
4	1.7450 ± 0.0686	2b
5	0.8443 ± 0.2005	*
6	1.5290 ± 0.2865	1a
7	0.6099 ± 0.1528	*
8	0.6376 ± 0.0515	*

* Deposit over copper strip

1a: the classification of the freshly polished strip is 1, the designation is slight tarnish, and the description is light orange, almost the same as a freshly polished strip

2b: the classification of the freshly polished strip is 2, the designation is moderate tarnish, and the description is lavender

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