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Determination of trace elemental sulfur and hydrogen sulfide in petroleum and its distillates by preliminary extraction with voltammetric detection

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Determination of elemental sulfur and hydrogen sulfide at sub-ppm levels in petroleum and its distillates was individually investigated using two convenient, accurate and sensitive procedures. These involved preliminary extraction of sample species, which were then detected by differential pulse polarography (DPP) and square wave voltammetry (SWV) on dropping mercury and static mercury drop electrodes, respectively. In one procedure, the required amount of sample was diluted with isopropyl alcohol–toluene (2 + 1 v/v) and was heated to 80 °C. Hydrogen sulfide available in the sample was then delivered through a designed system to an absorber cell by a controlled flow of helium gas in order for its concentration to be determined by SWV detection. In another procedure, an appropriate amount of sample was shaken with a recommended volume of extraction solution. The mixture was filtered in two steps and was then ready for its elemental sulfur content to be measured by DPP detection. The effects of extraction parameters such as volume ratio of extraction solution to sample, type of extraction solution and extraction time were studied in order to achieve a high recovery of sulfur. Various instrumental factors such as scan rate, pulse height, initial and final potential and purge time were optimized. The method was free from interferences from organic sulfides, disulfides and thiophene. The 3σ detection limits were 10 and 100 ng g^{-1} for H$_2$S (by use of SWV) and S^0 (by use of DPP), respectively. At a 1 µg g^{-1} level in samples, the relative standard deviations ($n = 4$) were 1.7 and 3.3% for SWV and DPP, respectively

1. Introduction

Elemental sulfur and hydrogen sulfide are the best known active sulfur species, and are the main causes of corrosion in oil facilities.[1,2] A great deal of care is exercised by petroleum refiners to minimize these species in their products. In the doctor sweetening method, free sulfur addition must be carefully controlled to avoid the production of a corrosive gasoline. Because of the corroding effect of the sulfur compounds remaining after the refining of petroleum on various metals,[3–7] poisoning of catalysts[8,9] and air pollution control,[10–13] it is extremely important to have analytical methods to detect and determine the most common sulfur compounds in the refining industry.

In surveying the literature for information pertaining to the qualitative and quantitative determination of elemental sulfur, it was found that several ASTM methods[14–16] make use of the copper strip corrosion test for detecting elemental sulfur. Another ASTM method[17] employs the mercury corrosion test to detect elemental sulfur. The most often used method for the quantitative determination of free sulfur in appreciable amount is the butanethiol or inverse doctor test described by Wirth and Strong.[18] In a study of methods for determining elemental sulfur, Ball[19] found the butanethiol test to be the best of the existing methods, but concluded that even this method was subject to inaccuracy when employed for low concentrations of elemental sulfur in hydrocarbons. Morris *et al.*[20] described a method for the quantitative determination of S^0 in aromatic hydrocarbons but it was satisfactory only for the range 0.1–20%. The general application of polarography to the determination of inorganic and organic compounds in pet-

rochemical analysis has been reported.[21,22] Usually, polarographic methods have been applied to the determination of sulfur compounds, using toxic solvents such as methanol and pyridine. Guinon *et al.*[23] studied the simultaneous determination of elemental sulfur, thiols and disulfides in petroleum naphtha by differential pulse polarography (DPP). A variety of methods are also available for the measurement of hydrogen sulfide in different matrices.[24–30] Unfortunately, there are few reliable, sensitive and precise methods for the measurement of H$_2$S and S^0 directly in petroleum with the possibility of application at or below µg g^{-1} levels. Several methods (colorimetric and potentiometric) have been proposed.[31–33] These methods are sensitive to the determination of elemental sulfur and hydrogen sulfide, but they are time consuming and tedious. Furthermore, the presence of certain constituents in the sample matrix makes accurate determination impossible.

In this paper, we describe a new procedure for the determination of H$_2$S and S^0 in petroleum and its distillates based on a preliminary extraction with voltammetric detection. This method offers several inherent advantages for H$_2$S and S^0 determination. Voltammetric detection methods are specific, since other species are electrochemically inactive at potentials where H$_2$S and S^0 are detected. Also, these techniques are very sensitive. By use of square wave voltammetry (SWV) and DPP, detection limits (DLs) of 10 and 100 ng g^{-1} are obtained, respectively. The DL can be improved for more demanding applications with increasing amount of the sample and by applying differential pulse stripping voltammetry (DPSV) as a detection mode. Here, two procedures for the determination of hydrogen sulfide and elemental sulfur are described.

2. Experimental

2.1. Chemicals

The extraction solution was prepared as a 0.03 M H_2SO_4 solution in light petroleum–toluene–ethanol (2.8 + 1.2 + 1) which was purged by passing helium gas through the solution for 5 min. This solution was used in DPP as the supporting electrolyte for the determination of elemental sulfur. A stock standard solution of crystalline sulfur in the supporting electrolyte was used as an S^0 standard (*ca.* 1000 µg g⁻¹; Merck, Darmstadt, Germany). Also, a stock standard solution of sodium sulfide, $Na_2S·9H_2O$ (*ca.* 1000 µg S g⁻¹, Merck) in the supporting electrolyte (0.5 M KOH, Aldrich, Milwaukee, WI, USA) was used and standardized iodimetrically daily.[34] All solvents were used without further treatment.

Caution. H_2S is a foul smelling, very toxic and dangerous gas. Its smell is noticeable at 0.02 ppm but the gas tend to anaesthetize the olefactory senses and the intensity of the smell is therefore a dangerously unreliable guide to its concentration, H_2S causes irritation at 5 ppm, headaches and nausea at 10 ppm and immediate paralysis and death at 100 ppm.

2.2. Apparatus

Fig. 1 shows the apparatus for trace hydrogen sulfide determination in petroleum and its distillates. The apparatus used consisted of a 250 or 500 ml reaction flask thermostated at 80 °C. An acid reservoir with a capacity of 50 ml of (1 + 2) HCl was attached to the mouth of the reaction flask. A 100 ml gas washing bottle containing 0.5 M KOH aqueous solution was used as H_2S absorber. The absorber was sealed by a sintered glass stopper (porosity No. 2). This was done in order to increase the contact surface area contact between the gas and the

solution. The detector consisted of an EG&G Princeton Applied Research (PARC) (Princeton, NI, USA) Model 303A static mercury drop electrode (SMDE), controlled by a PARC Model 384B potentiostat. The Ag/AgCl reference electrode filling solution was 3 M KCl saturated with silver ions, supplied by PARC. A platinum wire was used as the counter electrode.

2.3. Procedure

Procedure A. The required amount of sample (petroleum or its distillates) was weighed in a 500 ml beaker and diluted with isopropyl alcohol–toluene (2 + 1) according to Table 1. The contents were transferred completely with a further amount of the mixture into the reaction vessel. The gas washing bottle was filled with 35 ml of 0.5 M potassium hydroxide solution and the apparatus was set up as shown in Fig. 1. Helium gas was passed through the system at 1 L min⁻¹ as the carrier gas. The reaction mixture was heated to about 80 ± 2 °C by using a thermostated mantle. A 30 ml volume of (1 + 2) HCl was slowly added to the reaction mixture when the temperature reached 80 °C. After an extraction time of 1 h, the heating and the gas flow to the system were stopped. It was observed that during this period, part of the solvent and light petroleum fractions were distilled and condensed in the absorber cell (gas washing bottle), and other part left the system to waste. The contents of absorber were transferred to a separating funnel in order to separate the two phases. The aqueous phase was transferred into a 50 ml calibrated flask and then diluted to volume. The polarographic analyzer was set up under optimized instrumental conditions to determine the hydrogen sulfide content by using SWV on a static mercury drop electrode (SMDE). Results obtained were compared with calibration graph, plotted using freshly prepared standard solutions.

Procedure B. The required amount of sample was weighed in a calibrated flask (50–200 ml). The recommended volume of extraction solution as described in Table 1 was added to the contents of the flask. The mixture was shaken for 30 min by using a shaker and then filtered using a Whatman No. 52 filter-paper. The filtrate was diluted with a suitable volume of the extraction solution in a calibrated flask. The solution was then filtered by using a 0.2 µm membrane filter before injection into the polarographic cell. Calibration graphs were prepared daily using the standard addition technique and DDP as a detection mode on a dropping mercury electrode (DME).

3. Results and discussion

3.1. Principles of detection

Hydrogen sulfide and elemental sulfur were determined by using a combination of extraction and voltammetric techniques. Extraction of hydrogen sulfide from petroleum and its distillates was performed thorough the distillation of a specified mixture at 80 °C as prescribed in procedure A. In order to increase the extraction efficiency and to have a shorter extraction time, it

Fig. 1 Apparatus for determination of trace hydrogen sulfide in petroleum and its distillates.

Table 1 Sample weights recommended for SWV and DPP detection

Concentration range/µg g⁻¹ sulfur		Sample size/g		Volume of diluent/ml	
Elemental sulfur	Hydrogen sulfide	SWV	DPP	SWV	DPP
—	0.01–0.10	150–20	—	90–60	—
0.1–1.0	0.10–1.00	20–2	50–20	60–30	40
1.0–10	1.00–10.0	2–0.5	20–5	30–15	30
10–100	10.0–50.0	0.5–0.05	5–1	15	20
>100	>50.0	By dilution	By dilution	15	20

was necessary to purge the sample by an inert gas as a carrier and acidify the medium during the distillation process. The polarographic determination of sulfide has been well documented.[35–37] As with other substances which form slightly soluble or complex compounds with mercury, sulfide ion in a strongly alkaline medium produces a well-defined anodic wave. This corresponds to the oxidation of mercury to mercuric sulfide. The mechanism of the reaction in strongly alkaline medium, with the half-wave potential 0.76 V *vs.* SCE, is

$$Hg + HS^- + OH^- \rightleftharpoons HgS + H_2O + 2e^- \qquad (1)$$

Owing to the analytical advantages of SWV for reversible reactions, this technique for sulfide ion measurements was perfected in this work as a detection mode under optimized conditions. Elemental sulfur was extracted from the sample by mixing and shaking it with extraction solution. The mixture was then filtered in two steps (using paper and membrane filters) and the filtrate was transferred to the polarographic cell for determination of S^0 by a voltammetric technique.

No report was found in the literature of the use of the DME for the analytical measurement of oxidation reactions of elemental sulfur. Although in an anodic scan elemental sulfur is irreversibly oxidized to its oxidized species such as sulfurous and sulfuric acid, it offers an inherent advantage for elemental sulfur measurement. Since the interference of certain constituents in the sample matrix (*e.g.*, thiols and disulfides) which are electrochemically active near the peak potential of elemental sulfur is removed, in the present work anodic DPP was therefore used in S^0 measurements.

3.2. Response characteristics

The response and sensitivity of the methods were studied using alkaline sodium sulfide and crystalline sulfur standards in the supporting electrolyte solution. Detection limits of 10 and 100 ng g^{-1} were calculated at 3σ for S^{2-} and S^0 measurements, respectively, where σ is the estimated standard deviation for triplicate blank measurements. Further improvement in the detection limit is possible using multiple or larger sample sizes, differential pulse cathodic stripping voltammetry (DPCSV), and also by decreasing the cell volume. SWV and DPP are usually more reproducible with an adequate sensitivity and require less time per determination than DPCSV. In previous work,[38,39] the determination of trace total sulfur in organic compounds by Raney nickel reduction with non-dispersive SO_2 detection and with DPCSV as a sulfide detection mode was reported. With DPCSV a decrease in peak height (5–20%) was observed for successive measurements of the same solution in the polarographic cell. Apparently, a significant fraction of the sulfide concentration in the bulk solution is depleted during the deposition–measurement process. Accurate sulfur determination was obtained only by using the initial measurement of a freshly desulfurized sample. In the present work, this effect was not observed when using SWV detection.

The calibration graph obtained from analytical results for hydrogen sulfide shows that by using SWV, the sensitivity is 6 nA (ng g^{-1})$^{-1}$ and the dynamic range extends to 275 times the detection limit. With SWV the response is linear to about 10 µg S g^{-1} whereas with DPP the response is linear over the range 0.5–150 µg S g^{-1}. Above 150 µg S g^{-1} in the sample, the response becomes non-linear, as shown in Fig. 2. Non-linearity is probably due to the onset of multilayer surface coverage and the resulting change in the electrode mechanism.[40] The sensitivity is 300 nA (µg g^{-1})$^{-1}$ and the dynamic range extends to 750 times the detection limit in S^0 measurement. Comparison of the slopes of the graphs shows that under the optimum conditions, SWV (in the determination of sulfide ion) is 20 times more sensitive than DPP (in the determination of S^0). For hydrogen sulfide and elemental sulfur, the precision calculated

from the relative standard deviation of four replicate determinations was 1.7 and 3.3%, respectively, for a sample containing 1.0 µg S g^{-1}.

3.3. Optimization of detection conditions

Table 2 shows the optimized typical parameters in SWV and DPP detection. In SWV, the peak current and pulse height are linearly related up to 0.08 V with a frequency of 120 Hz and a scan rate of 240 mV s^{-1}. When the concentration of sulfide is 4.6 µg g^{-1} for a pulse height greater than 0.08 V, widening and splitting of the peaks occurs. With increasing pulse frequency, the double layer electric formed around the surface of the electrode is rapidly destroyed and the charging current is substantially decreased. When using an instrument such as a Model 384B polarographic analyzer, multiple scans are performed on a sample. The signal-to-noise ratio increases as the square root of the number of scans averaged. Scanning at a rate faster than the kinetics of the faradaic process causes the current to be controlled kinetically instead of diffusionally. The peak height may therefore not be directly proportional to concentration. The scan rate (v) and drop time (τ) are inversely related. If τ becomes very small, *i.e.*, less than ~ 1 ms, the capacitance current caused by the pulse applied would not decay completely.

It was observed that the slop of the calibration graph in DPP became 20 times lower than the slope in SWV. The decrease in slope was caused by an increase in the viscosity of solution or
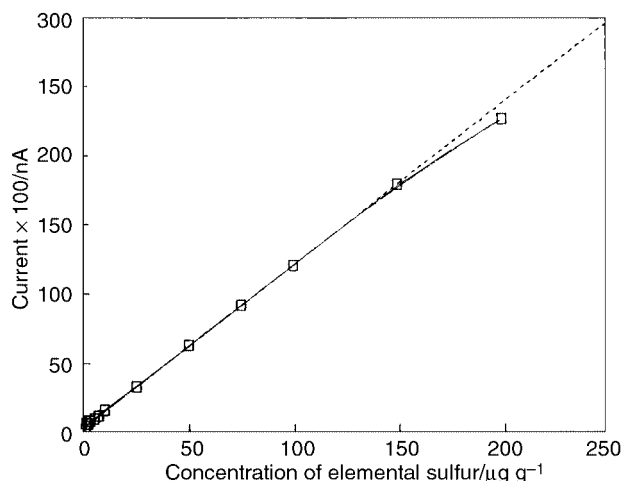

Fig. 2 Sulfur calibration using DPP. $E_i = -0.40$ V; pulse height, 0.05 V; equilibrium time, 10 s; purge time, 60 s; scan rate, 5 mV s^{-1}; anodic scan.

Table 2 Typical instrumental parameters for analysis using SWV and DPP detection

Optimized parameter	Detection mode	
	SWV[a]	DPP[b]
Pulse height/V	0.07	0.05
Scan increment/mV	2	5
Scan rate/mVs^{-1}	240	5
Initial potential/V	−1.00	−0.60
Final potential/V	−0.4	0.00
Frequency[c]/s^{-1}	120	—
Purge time/s	240	60
Equilibrium time/s	5	10
Drop time[d]/s	—	1
Supporting electrolyte	0.2 M KOH	0.03 M H$_2$SO$_4$

[a] Specific for hydrogen sulfide detection. [b] Specific for elemental sulfur detection. [c] Not available in DPP detection mode. [d] SWV was used in SMDE for the detection of sulfide.

change in the size of the solvated species. Since the peak potential (E_p) in both detection modes is a function of the total ionic strength of the solution, E_p was then shifted to a more negative value on increasing the concentration of the supporting electrolyte. It was also observed that when an excess of supporting electrolyte was present in the solution, the peak current was significantly decreased.

3.4. Recovery of H₂S and S⁰ from petroleum and its distillates

Extraction of hydrogen sulfide from petroleum with different viscosities depends greatly on the experimental conditions such as extraction time, pH, flow rate of the carrier gas and temperature of the reaction cell. Because of the volatility of H₂S and conversion of the gas to organosulfur compounds (thiol and polysulfide species), a decrease in its concentration is observed. The most accurate determination of hydrogen sulfide is usually obtained from on-line analysis of petroleum and its distillates. In cases where there is no possibility of on-line measurement of this compound, sampling and storage should be performed according to international standards.[41,42]

In order to study the effect of the experimental conditions on the average recoveries of hydrogen sulfide, a suitable sample blank was prepared with the same matrices as in petroleum samples. To prepare this sample, a petroleum with an H₂S content of less than 10 µg g⁻¹ and a total sulfur content of less than 0.5 wt.% was first selected. The sample was then stripped by passing helium at 4 l min⁻¹ through the reaction vessel at the temperature of 80 °C and a stripping time of 120 min. The standards were prepared by addition of an exact weighed amount of zinc sulfide to the sample blank and mixed thoroughly. Hydrochloric acid was then slowly added to the

reaction vessel and the released hydrogen sulfide was carried to the absorber cell through the petroleum matrix by helium.

Table 3 shows the effect of the experimental conditions on the recovery of 93 µg g⁻¹ hydrogen sulfide (as sulfur) in different steps with SWV detection. The average recovery in each step was obtained from the average of triplicate measurements with a 95% confidence limit. Increasing the extraction time over 60 min did not have any appreciable effect on the recovery. It was found that the temperature and helium flow rate had more effect than other parameters on the recovery. The best step to achieve to a good recovery of H₂S is related to step 5 (Table 3).

Direct determination of hydrogen sulfide in petroleum distillates by potentiometric titration and voltammetric techniques is well known.[29,33] It is impossible to apply these methods to petroleum, since the surfaces of the electrodes are coated by asphaltenic species. The designed extraction system shown in Fig. 1 significantly removes the interferences before the measurement step. Table 4 shows the results obtained for H₂S determination from 17 standard samples in a wide range of concentration using preliminary extraction of H₂S with electrochemical measurements. Average recoveries of 99.5 and 98.6% were calculated with a confidence limit of 95% for the voltammetric and potentiometric titration methods, respectively. In voltammetric detection, separation of two phases from each other in the absorber cell caused a small decrease in recovery before the measurement step. For petroleum distillates, it was possible to detect hydrogen sulfide and elemental sulfur simultaneously using voltammetric techniques. In this case preliminary extraction of these species was not required. In the case of extraction of elemental sulfur from petroleum, the recovery was approximately 80–85%. Therefore, the standard addition technique was ideally suited for the determination of trace elemental sulfur in petroleum. It was observed that for

Table 3 Effect of experimental conditions on recovery of hydrogen sulfide

Experimental conditions	Recovery[a] (%)					
	45.0 Step 1	82.5 Step 2	90.0 Step 3	98.8 Step 4	98.6 Step 5	92.0 Step 6
Time of extraction/min	180	120	120	120	60	45
Reaction cell temperature/°C	50	70	80	80	80	80
Flow rate of carrier gas/ml min⁻¹	300	500	500	1000	1000	1000
Ratio of propan-2-ol to toluene	3 + 2	3 + 2	2 + 1	2 + 1	2 + 1	2 + 1

[a] The results were obtained under the optimized instrumental conditions in Table 2 with SWV detection.

**Table 4** Recovery of hydrogen sulfide from petroleum and its distillates

Calculated concentration/ µg g⁻¹ sulfur	Average observed concentration[a]/ µg g⁻¹ sulfur	RSD[a] (%)	Average observed concentration[b]/ µg g⁻¹ sulfur	RSD[b] (%)	No. of determinations	Recovery[c] (%)	
						By potentiometry	By SWV
1066	1086	1.8	1059	0.2	3	101.8	99.3
1053	1056	0.3	—	—	3[a]	100.3	—
895	880	1.7	876	0.5	4	98.3	97.9
615	625	2.4	610	0.4	4	101.6	99.2
437	427	3.2	—	—	4[a]	97.7	—
484	494	2.8	475	0.5	3	102.1	98.1
112	110	1.8	108	0.8	3	98.2	96.4
111	107	3.7	—	—	2[a]	96.4	—
99.0	99.0	3.0	97.5	1.0	3	100.0	98.5
48.7	48.0	1.5	—	—	2[a]	98.6	—
48.0	50.0	4.4	49.0	0.9	4	104.2	102.1
16.5	16.0	4.4	—	—	4[a]	97.0	—
13.2	13.0	3.9	12.9	1.2	3	98.5	97.7
2.20	2.30	4.3	—	—	2[a]	104.5	—
3.10	2.90	6.5	3.05	1.0	3	93.5	98.4
1.30	1.60	12.5	1.32	1.5	4	Unreliable	101.5
0.50	—	—	0.48	3.2	4[b]	—	96

[a] Potentiometric titration method. [b] SWV. [c] The results were obtained under the optimized instrumental and experimental conditions in Tables 2 and 3.

Table 5 Determination of hydrogen sulfide and elemental sulfur in different petroleum and distillate samples

| No. | Sample | SWV detection[a] | | Potentiometric titration[a] | | DPP detection[b] | |
		H_2S concentration/μg g^{-1}	RSD (%)	H_2S concentration/μg g^{-1}	RSD (%)	S^0 concentration/μg g^{-1}	RSD (%)
1	Omidieh	12.5	1.4	12.9	4.9	3.4	2.6
2	Ahwaz	24.4	0.8	26.1	4.4	35.5	1.5
3	TA 75	111.3	0.5	113.8	1.6	11.0	1.8
4	Distillate 1[c]	0.2	3.1	—	—	0.55	3.7
5	Distillate 2[c]	0.09	3.9	—	—	0.20	4.5

[a] Mean $\pm$ s, $n = 3$. [b] Used in standard addition mode. [c] Not detectable by potentiometry.
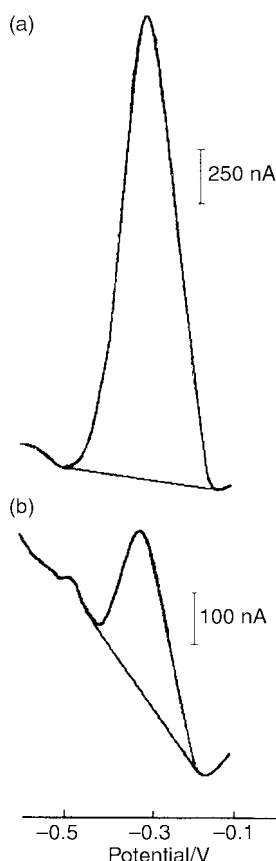
Fig. 3 Differential pulse polarograms of (a) a petroleum sample and (b) sample as in (a) + 50 μg g^{-1} sulfur.

standard solutions, the peak potential was gradually shifted from −0.15 to −0.30 V with increasing elemental sulfur concentration; this effect is probably due to the higher solution viscosity. For petroleum samples, the peak potential of elemental sulfur appeared at about −0.30 V. This was confirmed by the position of the peak when a certain amount of standard solution was added to the sample, as shown in Fig. 3. It was observed that trace amounts of sulfur (< 1 μg g^{-1}) decreased the peak height to about 15–20% by DPP for successive measurements of the same solution. Therefore, accurate sulfur determination was obtained only by using the initial measurement of a freshly extracted sample.

3.5. Determination

Table 5 shows the results obtained from determination of hydrogen sulfide and elemental sulfur in several samples of Iranian petroleum and distillates. These results are compared with another reliable and sensitive method, potentiometry. Owing to the impossibility of direct H_2S measurement in a petroleum matrix by potentiometry, a pre-extraction was applied according to procedure A and by using the designed system shown in Fig. 1. By using commercial automatic potentiometers, it is possible to achieve a detection limit of 1 μg g^{-1} by selection of a sample weight $\geqslant$150 g. No reference was found in the literature to compare the results obtained in this work for the determination of S^0 at trace levels especially in petroleum matrices. Light thiols with boiling-points lower than 80 °C were extracted in the absorber cell containing 0.2 M potassium hydroxide (Fig. 1). The position of the RSH peak was detected at −0.55 V in SWV, which is approximately 0.2 V further than the H_2S position. This was due to oxidation of mercury in the presence of mercaptan species according to the reversible reaction

$$RSH + Hg \rightleftharpoons RSHg + H^+ + e^- \tag{2}$$
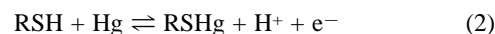
In DPCSV, a related peak was observed at the same potential region (−0.55 V), but with a better resolution than in SWV. Hydrogen sulfide and thiol species can also be detected simultaneously in potentiometry with a 0.25 V difference in the end-points.

4. Future work

Future studies will be focused on the determination of total thiols and disulfides in petroleum and its distillates. Also, the construction of a new pyridine-free Karl Fischer reagent for the determination of sub-ppm levels of water in non-aqueous media by a coulometric method will be investigated.

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