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The S. W. Polarographic Determination of Disulfide, Mercaptan and Free Sulfur in Petroleum Naphtha

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The application of square-wave polarography to the determination of small amounts of disulfide, mercaptan and free sulfur in a mixed solution of methanol, glacial acetic acid, and sodium acetate was studied. Disulfide, mercaptan, and free sulfur in concentrations below 10 ppm were easily determined in these mixed solvents. The derivative wave heights were proportional to the concentrations predicted by the theory of s. w. polarography. The effects of changes in solvent and in supporting electrolyte concentration, dissolved oxygen, and temperature were discussed. It was determined that concentrations of 2 vol% glacial acetic acid and 1.4 M sodium acetate were necessary to obtain a constant peak height. The temperature coefficients of disulfide, mercaptan and free sulfur were about 4.5 (first wave), 0.7 and 4.5% per degree respectively in the neighborhood of 25°C. The effect of the dissolved oxygen was removed by passing nitrogen through for 5 min.

In previous papers,[1,2] we have reported a s.w. polarographic determination of mercaptan compounds and free sulfur in petroleum naphtha, and the spectrophotometric determination of thiophene in petroleum naphtha with α-nitroso-β-naphthol. Because the effect of sulfur compounds on the refinery process and on the product quality varies widely with the type of sulfur compound, it is important to have analytical methods to detect and determine the sulfur compound types most common in the petroleum industry. Therefore, the s.w. polarographic method for the determination of small amounts of disulfide, mercaptan and free sulfur has been developed; in it the sample is dissolved in a mixed solution of 2 vol% of glacial acetic acid, 98 vol% of methanol, and 1.4 M of sodium acetate, and the solution is polarographed. The polarographic waves of disulfide consisted of two waves; the peak potential for the first wave was -0.35 V *vs.* SCE, while that of the second wave was -0.53 v *vs.* SCE. The peak potentials of the mercaptan compound and free sulfur were -0.35 and -0.54 V *vs.* SCE respectively. The time required for an analysis was only 30 min.

The presence of hydrogen sulfide, thiophene, and monosulfide had no influence on either the peak potential or the wave height. The limit of determination was governed by the solubility of naphtha in the base solution.

This method has a higher sensitivity than conventional polarography; it is affected by an irreversibly-reducible material, such as oxygen, in the measurement of disulfide, mercaptan, and free sulfur.

1) M. Kashiki and K. Ishida, *Rev. of Polarography*, **12**, 169 (1964).
2) M. Kashiki and K. Ishida, This Bulletin, **39**, 642 (1966).

Experimental

Apparatus and Reagent. A Yanagimoto, Model PA-102, recording polarograph and a PM-1 multiplier attachment were used. A polarographic H-type cell with a saturated calomel electrode was also used. A large capacitor (2000 μF electrolytic) was connected between the SCE and a platinum electrode in order to minimize any resistance effects.[1] The capillary constants in an open circuit (h=61.0 cm) were t=3.8 second and m=2.721 mg per second.

All experimental measurements were made in an air-conditioned room with the temperature held constant at 25 ± 0.1°C. Twenty-milliliter flasks were used to dilute the sample with a mixed solution of the electrolyte solvent.

Wako's methanol, glacial acetic acid, and sodium acetate were used. All the reagents and chemicals used were of commercial extra-pure grade or of analytical-reagent grade; their purities were examined beforehand polarographically.

The Preparation of Copper Powder.

Cupric sulfide	crystal, reagent grade
Zinc metal	powder, reagent grade
Hydrochloric acid	reagent grade, 2 N
Acetone	reagent grade, redistilled

Dissolve 90 g of copper sulfate crystals in 1 *l* of cold, distilled water containing 40 m*l* of 2 N hydrochloric acid. Prepare a thick slurry of 30 g of pure zinc powder in 50 m*l* of water containing a small amount of wetting agent, and slowly stir into this the copper sulfate solution. Continue to stir until the precipitated copper turns from a red to a red-brown color. This copper is washed with distilled water; the water is replaced with acetone and then with ether. Red-brown copper was kept in a vacuum in a dried condition. Completely-dried copper powder is quite stable in air.

TABLE 1. DETERMINATION OF MERCAPTAN AND FREE SULFUR IN THE PRESENCE OF DISULFIDE

Sample No.	Taken			Found		
	Disulfide ppm	Mercaptan ppm	Free sulfur ppm	Disulfide ppm	Mercaptan ppm	Free sulfur ppm
1	10	1.8	1.0	8	1.6	1.3
2	15	3.0	2.5	11	2.8	2.8
3	32	6.5	4.0	29	6.8	4.2
4	87	18.0	8.5	82	17.8	8.5
5	155	28.5	14.0	157	28.5	14.0
6	285	60.0	29.5	281	60.6	29.0

The Preparation of the Copper Column. In this work, a column with a bed volume of 20 m*l* of copper powder in a glass tube, 2 cm in diameter and 25 cm long, was used. The size of the column could be adjusted depending on the quantity of sulfur compound.

Procedure. To a 25 m*l* volumetric flask, add 10 m*l* of a 1.4 M sodium acetate methanolic solution and 0.5 m*l* of glacial acetic acid; then stir until all have been dissolved. Pipet 1 m*l* of petroleum naphtha sample into this volumetric flask. Dilute to the volume mark with methanol. Mix the solution thoroughly. Transfer the solution to the polarographic cell and deaerate with high-purity nitrogen for at least for 5 min. Scan from −0.25 to −0.65 V *vs.* SCE at a suitable sensitivity setting of the polarograph.

When free sulfur exists with mercaptan and when disulfide is present in petroleum naphtha sample, first the total peak height of the solution at −0.35 and −0.54 V *vs.* SCE was measured; then the solution was slowly passed through a red-brown copper column and the peak height of the filtrate was measured again when disulfide was not removed at room temperature.[3] The peak height of the filtrate corresponds to the amount of the disulfide. The amounts of mercaptan and free sulfur can be calculated by subtracting the peak height of the disulfide from the total peak height of the original solution at −0.35 and −0.54 V *vs.* SCE.

Mercaptan and free sulfur apparently reacted with copper, forming cuprous mercaptide, which is yellow-brown in color and which is not soluble in benzene, water dilute hydrochloric acid, or ammonia. These chemical properties of mercaptan suggest the formation of cuprous mercaptide.[4] The analytical results of the determination of their sulfur compounds are shown in Table 1. The agreement is quite satisfactory.

Calibration Curve. The calibration curves shown in Figs. 1 and 2 were obtained by the procedure using standard disulfide, mercaptan, and free sulfur solutions of known concentrations. As may be seen in Figs. 1 and 2, the peak height and the concentration showed a good linear relationship.

Disulfide. A known amount of a standard solution of disulfide (*i-Amyl disulfide*) was added to the mixture of 2 vol% of glacial acetic acid, 98 vol% of methanol, and 1.4 M of sodium acetate in a 25 m*l* volumetric flask. An aliquot of the solution was taken in a cell and polarographed after deaeration. The calibration curves obtained by these procedures are shown in Fig. 1. The detectable limit of the concentration of disulfide was about 10 ppm.

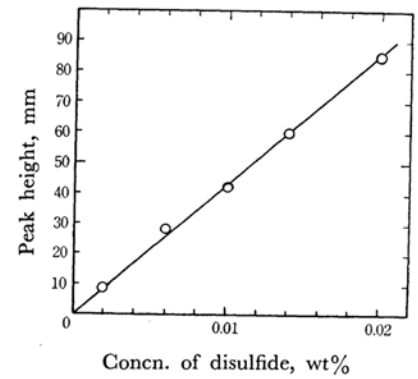


Fig. 1. Calibration curve of disulfide.
Parallel capacitance: 50 μF, Recorder sens.: 0.02 μA/mm., Amplifier sens.: 1/20, Gate: 1—9, Time constant: 41, S. W. Volt. adjust.: 20 mV.

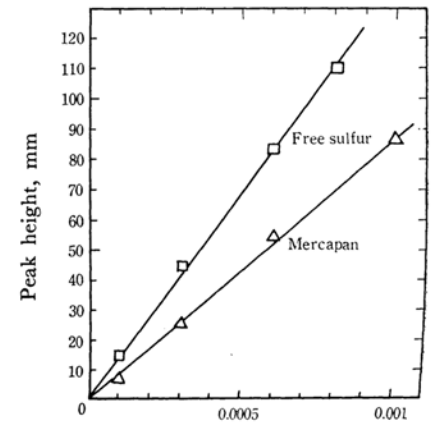


Fig. 2. Calibration curve of mercaptan and free sulfur.
Parallel capacitance: 50 μF, Recorder sens.: 0.02 μA/mm., Amplifier sens.: 1/20 (mercaptan), 1/50 (free sulfur), Gate: 1—9, Time constant: 41, S. W. Volt. adjust.: 20 mV.

3) M. Blumer, *Anal. Chem.*, **26**, 1039 (1957).
4) W. Ando, K. Sugimoto and S. Oae, This Bulletin, **36**, 477 (1963).

Mercaptan (n-Butyl Mercaptan) and Free Sulfur. The procedures for these substances are the same as those in the case of disulfide (see Fig. 2).

The detectable limit of the concentration of mercaptan and free sulfur was about 0.5 ppm.

Results and Discussion

Polarogram. *Disulfide.* The disulfide used were di-*n*-propyl, di-*n*, *i*, *t*-butyl, di-*n*, *i*-amyl, diphenyl, benzyl disulfide, and so on. Their purity was examined beforehand polarographically. The polarographic wave of disulfide consisted of two steps; the peak potential for the first wave was −0.35 V *vs.* SCE, while that of the second wave was −0.53 V *vs.* SCE (see Fig. 3).

Mercaptan. The mercaptans used were ethyl, *n*, *t*-propyl, *n*, *i*, *t*-butyl, *n*, *i*-amyl, *n*, *t*-octyl, laulyl, phenyl, benzyl mercaptan, and so on. Their purity was examined beforehand polarographically. The peak potentials of these compounds covered −0.25 to −0.45 V *vs.* SCE. An s. w. polarogram of 20 ppm of *n*-butyl mercaptan in the solution of 2 vol% of glacial acetic acid, 98 vol% of methanol, and 1.4 M of sodium acetate is given in Fig. 3.

Free Sulfur. Free sulfur was twice recrystallized by employing carbon disulfide and methanol. Its peak potential covered −0.49 to −0.60 V *vs.* SCE (see Fig. 3).

The Effect of the Reagent Concentration. In order to study the effect of the concentration of glacial acetic acid and sodium acetate, the peak height and the peak potential were measured at various concentrations of glacial acetic acid and sodium acetate, using as a standard petroleum naphtha.

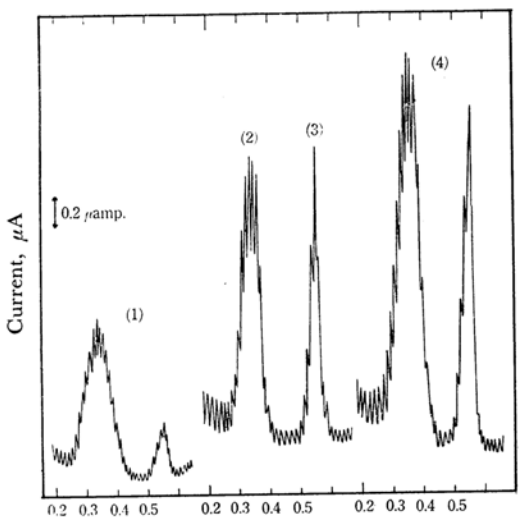


Fig. 3. S. W. Polarographic waves of disulfide, mercaptane and free sulfur in methanol, glacial acetic acid and sodium acetate mixture.
(1) 0.01 wt% disulfide (*i*-amyl disulfide), (2) 0.002 wt% mercaptan (*n*-butyl mercaptan), (3) 0.002 wt% free sulfur, (4) (1)+(2)+(3). Parallel capacitance: 50μF, Recorder sens.: 0.02 μA/mm, Amplifier sens.: 1/200, Time constant: 41, Gate: 1—9, S. W. Volt. Adjust: 20 mV.

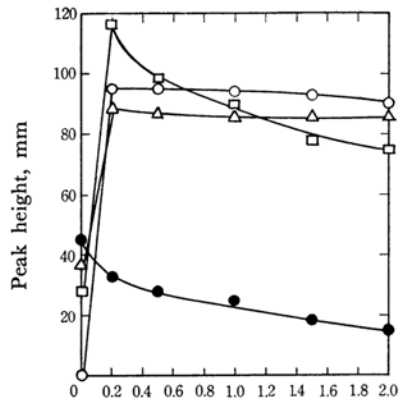


Fig. 4. Variation of the peak height with the glacial acetic acid concentration.
Parallel capacitance: 50 μF, Recorder sens.: 0.02 μA/mm., Gate: 1—9, Time constant: 41, S. W. Volt. adjust.: 20 mV.
○ Disulfide (1st peak) } 0.02 wt%, amp
● Disulfide (2nd peak) } sens. 1/20
△ Mercaptan 0.002 wt%: amp. sens. 1/50
□ Free sulfur 0.002 wt%: amp. sens. 1/100

Figure 4 gives the relationship between the concentration of glacial acetic acid and the peak height of each sulfur compound. It is apparent that a concentration of 2 vol% of glacial acetic

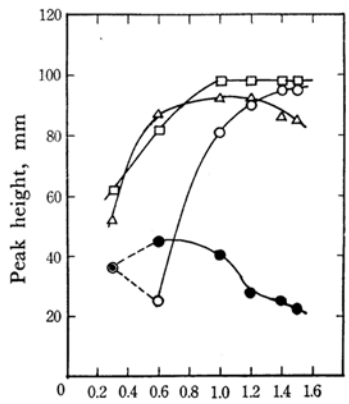
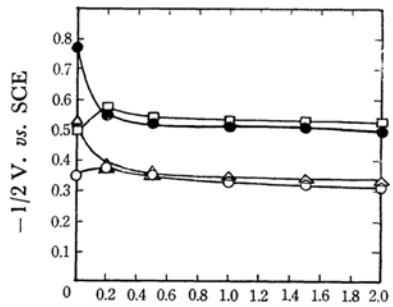


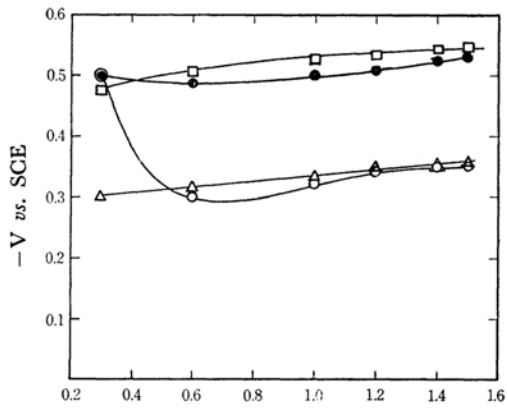
Fig. 5. Variation of the peak height with the sodium acetate concentration.
○ Disulfide 1st peak
● Disulfide 2nd peak
△ Mercaptan
□ Free sulfur
Figure 5 is otherwise under the same experimental condition as in Fig. 4.



Content of glacial acetic acid in ml/25 ml solvent

Fig. 6. Variation of the peak potential with the glacial acetic acid concentration.
○ Disulfide 1st peak
● Disulfide 2nd peak
△ Mercaptan
□ Free sulfur
Figure 6 is otherwise under the same experimental condition as in Fig. 4.

acid is necessary to obtain a constant peak height. Figure 5 gives the effect of the concentration of sodium acetate on the peak height of each sulfur compound. It may be seen that a concentration of 1.4 M of sodium acetate in necessary to obtain a constant peak height.



Concn. of sodium acetate, M

Fig. 7. Variation of the peak potential with the sodium acetate concentration.
○ Disulfide 1st peak
● Disulfide 2nd peak
△ Mercaptan
□ Free sulfur
Figure 7 is otherwise under the same experimental condition as in Fig 4.

Figures 6 and 7 give the relationships between the reagent concentration and the peak potential of each sulfur compound. It is apparent that the first wave of disulfide and the wave of mercaptan, and the second wave of disulfide and that of free sulfur coincided, respectively. Therefore, when free sulfur exists with the mercaptan compound, the true wave height of mercaptan can be obtained by deducting that of the first wave of disulfide from the total wave height.

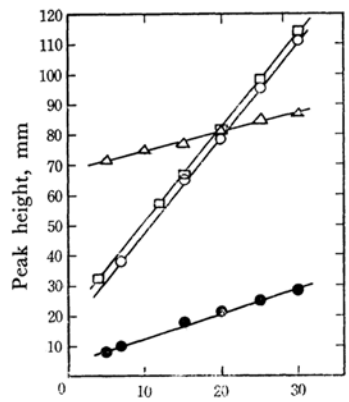
In the determination of disulfide, mercaptan, and free sulfur, therefore, the compositions of 2 vol% of glacial acetic acid and 1.4 M of sodium acetate were used, and the peak height measurements were made at −0.35 and −0.54 V *vs.* SCE.

Temperature Coefficient. *Disulfide (i-Amyl disulfide).* The polarographic wave of disulfide consisted of two waves, both of which increase as the temperature is raised. A plot of the wave height against the temperature yields a straight line, as is shown in Fig. 8. The temperature coefficients are about 4.5 (first wave) and 2.4 (second wave)% per degree in the neighbourhood of 25°C.

The concentration of disulfide in this study was 200 ppm.

Mercaptan (n-Butyl Mercaptan) and Free Sulfur. Mercaptan and free sulfur each showed one wave; both wave heights increase as the temperature is raised (see Fig. 8).

The temperature coefficient is about 0.7 and 4.5% per degree in the neighbourhood of 25°C. The concentration of mercaptan and free sulfur in this study was 20 ppm. The temperature had no effect upon the peak potential.



Temperature, °C

Fig. 8. The effect of temperature.
○ Disulfide 1st peak
● Disulfide 2nd peak
△ Mercaptan
□ Free sulfur
Figure 8 is otherwise under the same experimental condition as in Fig. 4.

The Effect of Dissolved Oxygen. The wave of dissolved oxygen overlaps with the waves of disulfide, mercaptan, and free sulfur in a mixed solution of 2 vol% of glacial acetic acid, 98 vol% of methanol, and 1.4 M of sodium acetate in s.w. polarograms. Therefore, it is necessary, for the

TABLE 2. RELATIVE ERROR IN THE DETERMINATION OF DISULFIDE, MERCAPTAN, AND FREE SULFUR

Disulfide (*i*-amyl disulfide)		Mercaptan (*n*-butyl mercaptan)		Free sulfur	
Concn. ppm	Percentage error, %	Concn. ppm	Percentage error, %	Concn. ppm	Percentage error, %
10.0	15.0	0.5	18.6	0.5	6.0
200.0	7.3	6.5	3.7	3.0	2.8
500.0	2.6	60.0	1.9	30.0	1.6

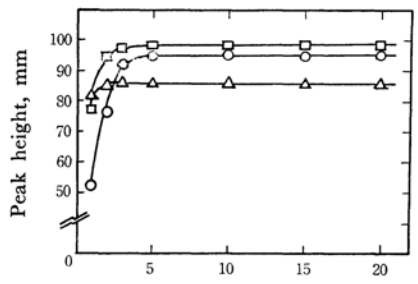


Fig. 9. The effect of dissolved oxygen.
○ Disulfide 1st peak
△ Mercaptan
□ Free sulfur
Figure 9 is otherwise under the same experimental condition as in Fig. 4.

determination of disulfide, mercaptan, and free sulfur, to remove the dissolved oxygen by passing nitrogen through for 5 min (see Fig. 9).

The results obtained by the proposed procedure are shown in Table 2.

Summary

An s.w. polarographic method for the determination of small amounts of disulfide, mercaptan, and free sulfur has been developed. This method seems to be the most useful one for disulfide, mercaptan, and free sulfur determination.

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