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The Square-Wave Polarographic Determination of Free Sulfur in Liquefied Petroleum Gases

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A method has been developed for the polarographic determination of the free sulfur present in liquefied petroleum gases in concentrations as low as 0.01 ppm. Samples of liquefied petroleum gases are collected in a specially-fitted pressure glass bottle. After the volatilization of the sample, the free sulfur remaining in the sample container is dissolved in a methanol - methyl iodide - glacial acetic acid - sodium acetate solvent, and the resulting solution is electrolyzed polarographically. The effect of the change in solvent and in supporting electrolyte concentration, dissolved oxygen and temperature are discussed. It is found that the concentrations of 90 vol% methanol, 2 vol% glacial acetic acid, 8 vol% methyl iodide, and 1.5 M sodium acetate are necessary to obtain satisfactory analytical results. The polarographic wave of free sulfur consisted of two waves; the peak potential of the first wave was -0.57 V *vs.* SCE, while that of the second wave was -0.87 V *vs.* SCE. The limit of determination was governed by the solubility of the naphtha in the base solution.

In previous papers,[1-3] we have reported a square-wave polarographic determination of mercaptan compounds and free sulfur in petroleum naphtha, the spectrophotometric determination of thiophen in petroleum naphtha with α-nitroso-β-naphthol, and the square-wave polarographic determination of disulfide, mercaptan, and free sulfur in petroleum naphtha.

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 for detecting and determining the sulfur compound types most common in the petroleum industry. Free sulfur in petroleum products presents a particularly important problem in the industry because of the ease with which it is formed and because of its corrosive nature. In contact with most metals, free sulfur reacts to form the metal sulfides.[4-6]

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[1] M. Kashiki and K. Ishida, *Rev. of Polarography*, **12**, 169 (1964).

[2] M. Kashiki and K. Ishida, This Bulletin, **39**, 642 (1966).

[3] M. Kashiki and K. Ishida, *ibid.*, **40**, 97 (1967).

[4] Am. Soc. Testing Materials, Designation D130-50T, " Tentative Method of Test for Free and Corrosive Sulfur in Petroleum Products."

[5] K. Uhrig and H. Levin, *Anal. Chem.*, **23**, 1334 (1951).

[6] G. E. Mapstone, *Ind. Eng. Chem., Anal. Ed.*, **14**, 107 (1942).

The corrosive action of free sulfur on mercury, copper, and silver has been used for some time as a semiquantitative test for sulfur in petroleum products. In the present study, the s.w. polarographic method for the determination of a small amount of free sulfur in liquefied petroleum gases has been developed; in it the sample is dissolved in a mixed solution of 2 vol% of glacial acetic acid, 90 vol% of methanol, 8 vol% of methyl iodide, and 1.5 M of sodium acetate, and the solution is polarographed.

The polarographic waves of free sulfur consisted of two waves; the peak potential for the first wave was −0.57 V *vs.* SCE, while that of the second wave was −0.87 V *vs.* SCE. The presence of hydrogen sulfide, mercaptan, and monosulfide had no influence on either the peak potential or the wave height. The limit of determination was governed by the amount of sample.

Experimental

Apparatus and Reagents. A Yanagimoto Model PA-102 recording polarograph with PM-1 multiplier attachment was used. A polarographic H-type cell with a saturated calomel electrode was used. A large capacitor (2000 μF electrolytic) was connected between the SCE and a platinum electrode in order to minimize the 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 the experimental measurements were carried out in an air-conditioned room with the temperature held constant at 25±0.1°C. Twenty-five-milliliter flasks were used to dilute the sample with the mixed electrolyte-solvent solution.

Wako's methanol, glacial acetic acid, methyl iodide, and sodium acetate were used. All the reagents and chemicals used were of a commercial extra-pure grade or of analytical-reagent grade; their purities were examined beforehand polarographically. Sulfur was twice recrystallized by employing carbon disulfide and methanol. As can be seen in Fig. 1, the sampling containers used were 500 m*l*, two-valved, glass pressure bottles (Taiatsu Glass Industry B-3).

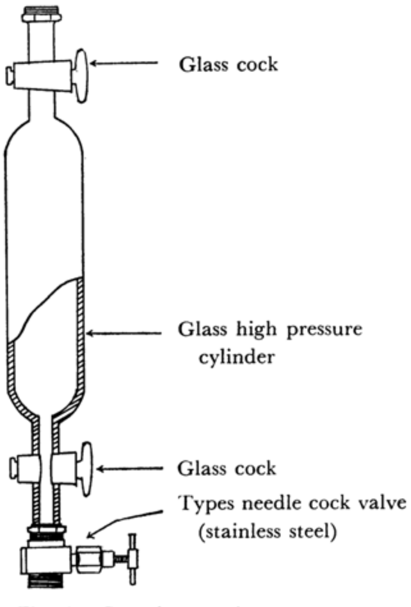


Fig. 1. Sample container.

Procedure. The glass pressure bottle filled with liquefied petroleum gases is weighed. Clamp the bottle in a vertical position and vent the gas slowly through the upper glass cock at room temperature. (Because of the flammability of liquefied petroleum gas, this operation should be carried out in a well-ventilated hood in the absence of fire.) Upon initial evaporation, the bottle cools, the vapor pressure in the bottle approaches 1 atom, and the glass cock may gradually be opened fully. The residue is then dissolved in 2 m*l* of methyl iodide and rinsed carefully with methanol into a 25 m*l* volumetric flask. A half milliliter glacial acetic acid and 1.5 mol sodium acetate are added, and the solution is diluted to the volume mark with methanol. The weight of the sample taken is determined by reweighing the partially-emptied glass pressure bottle. Mix the solution thoroughly. Transfer the solution to the polarographic cell and deaerate it with prepurified nitrogen saturated with a methanol solvent for a minimum of 3 min. Scan from −0.40 to −1.30 V *vs.* SCE.

From 2 to 3 hr are required for a single determination, of which some 30 min is the actual operating time.

Great care must be exercised in obtaining representative samples of liquefied petroleum gases for the determination of free sulfur. Some of the important factors which must be considered in the sampling procedure are considered below.

Air Oxidation of Hydrogen Sulfide. Hydrogen sulfide in hydrocarbon samples is readily oxidized to free sulfur by air and mild oxidizing agents. It is possible that this is the source of much of the free sulfur present in low-boiling hydrocarbon fractions. If the liquefied petroleum gas sample contains hydrogen sulfide, it is essential that all the air be expelled from the glass pressure bottle before it is filled. The sampling procedure makes allowance for flushing out the bottle with liquefied petroleum gas vapor. The air in the glass pressure bottle may, if desired, be replaced by nitrogen or helium gas before the sample is taken.

Nonvolatile Nature of Elemental Sulfur. As is shown above, free sulfur is essentially nonvolatile at room temperature. Upon evaporation, liquefied petroleum gas deposits the free sulfur which it contains. As sampling cocks in the field often have a deposit of sulfur around them, the sampling cocks and tubes must be flushed out thoroughly before the glass pressure bottle is attached to the sample source. It is likewise important that the sample be taken from the liquid and not the gas phase. In venting the glass pressure bottle before completely filling it, it is important that only a part of the liquefied petroleum gas in the glass pressure bottle be vented as a gas, and most of the material be vented as a liquid.

Corrosive Nature of Sulfide on Metals. Because free sulfur reacts with many metals, the sample container must be made of a material resistant to sulfur corrosion. A glass pressure bottle was found suitable for taking liquefied petroleum gas samples for the determination of free sulfur.

Results and Discussion

Polarogram. Free sulfur was twice recrystallized by employing carbon disulfide and methanol. Its purity was examined beforehand polarographically. The polarographic wave of free sulfur consisted of two waves; the peak potential of the first wave was −0.57 V *vs.* SCE, while that of the second wave was −0.87 V *vs.* SCE (see Fig. 2). In quantitative analysis, all the peak height measurements for this investigation were made at −0.87 V *vs.* SCE in order to obtain a stable peak height, which is more stabilized at this peak potential rather than at −0.57 V *vs.* SCE.

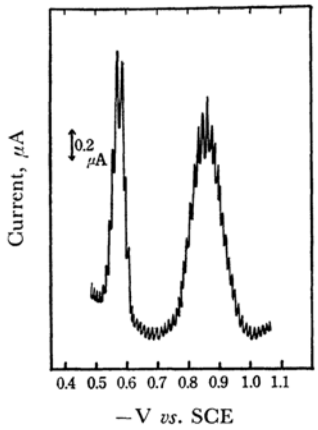


Fig. 2. Polarographic wave of free sulfur in methanol, glacial acetic acid, methyl iodide, and sodium acetate.
Parallel Capacitance: 50 μF, Recorder Sens.: 0.02 μA/mm, Amplifier Sens.: 1/200, Time Constant: 41, Gate: 1—9, S.W. Volt. Adjust.: 20.

Standardization. Prepare a standard solution of sulfur in methanol containing 25 mg of free sulfur per liter. Pipet 1 m*l* of this solution into a twenty-five-milliliter volumetric flask, add 1.5 M of sodium acetate, 0.5 m*l* of glacial acetic acid, and 2 m*l* methyl iodide, and dilute to the volume mark with methanol. Record a polarogram for this solution as outlined in the procedure above, and measure the peak current.

Calibration Curves. The calibration curves shown in Fig. 3 were obtained by a procedure using standard free sulfur solutions of known concentrations. As can be seen in Fig. 3, the peak height and the concentration were in a good linear relationship.

The Effect of the Reagent Concentration. In order to study the effect of the concentrations of glacial acetic acid, methyl iodide, and sodium acetate, the peak height and the peak potential of polarograms were measured at various concentrations of glacial acetic acid, methyl iodide, and sodium acetate, using standard liquefid petroleum gas. Figure 4 gives the relationship between the concentration of glacial acetic acid and the peak height of free sulfur. It is apparent that a concentration of 2 vol% glacial acetic acid is necessary to obtain a constant peak height. Figures 5 and 6 show the effect of the concentrations of sodium acetate and methyl iodide on the peak height of free sulfur. It may be seen that concentrations of 1.5 M of sodium acetate and 8 vol% of methyl iodide are necessary to obtain a stable peak height.

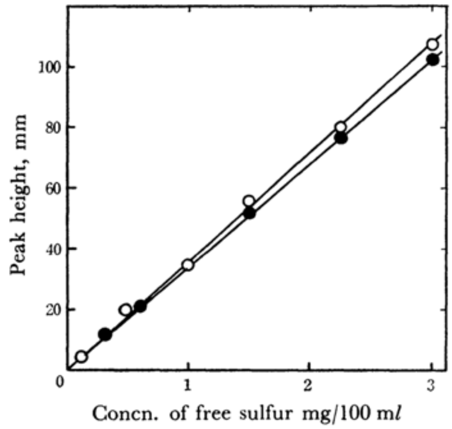


Fig. 3. Calibration curve of free sulfur.
Paraller Capacitance: 50 μF, Recorder Sens.: 0.02 μA/mm, Amplifier Sens.: 1/20, Gate: 1—9, Time Constant: 41, S.W. Volt. Adjust.: 20.
○: first peak, ●: second peak

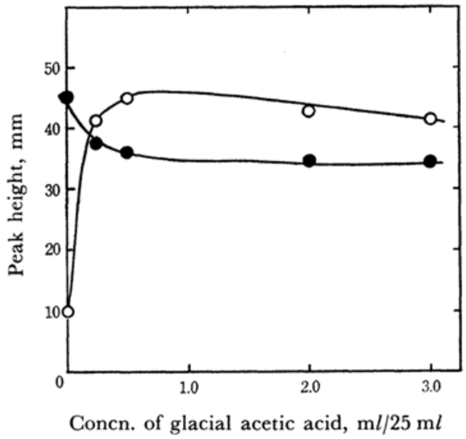


Fig. 4. The relation between concentration of glacial actic acid and peak height.
Parallel Capacitance: 50 μF, Recorder Sens.: 0.02 μA/mm., Gate: 1—9, Time Constant: 41, S.W. Volt. Adjust.: 20.
○: first peak, ●: second peak
Sample: Free sulfur 25 ppm

Figures 7, 8, and 9 give the relationships between the reagent concentration and the peak potential of free sulfur. In the determination of free sulfur, compositions of 2 vol% of glacial acetic acid, 1.5 M

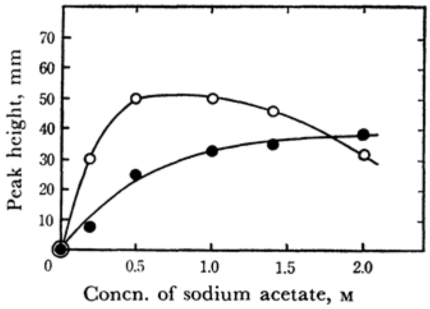
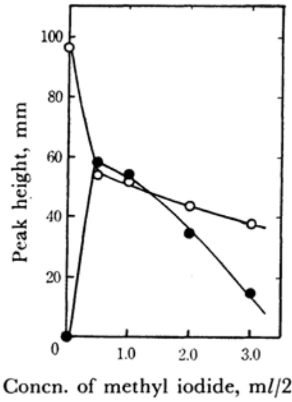


Fig. 5. The relation between concentration of sodium acetate and the peak height.
○: first peak, ●: second peak
The experimental conditions in Fig. 5 were the same as those in the case of Fig. 4.



Fit. 6. The relation between concentration of methyl iodide and the peak height.
○: first peak, ●: second peak
The experimental conditions in Fig. 6 were the same as those in the case of Fig. 4.

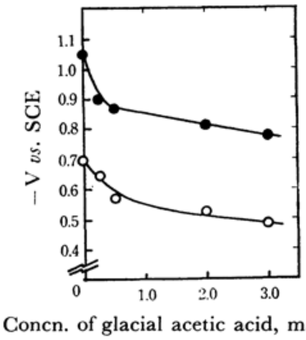


Fig. 7. The relation between concentration of glacial acetic acid and peak potential.
○: first peak, ●: second peak
The experimental conditions in Fig. 7 were the same as those in the case of Fig. 4.

of sodium acetate, and 8 vol% of methyl iodide were used.

Temperature Coefficient. The polarographic wave of free sulfur 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. 10. The temperature coefficients are 4.0 (first wave) and 2.3 (second wave) % per degree in the neighborhood of 25°C. The concentration of free sulfur in this study was 15 ppm.

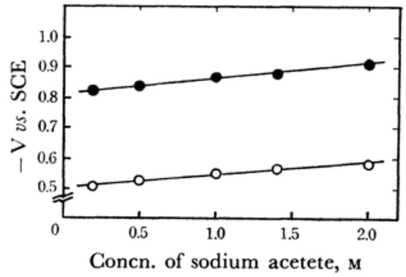


Fig. 8. The relation between concentration of sodium acetate and peak potential.
○: first peak, ●: second peak
The experimental conditions in Fig. 8 were the same as those in the case of Fig. 4.

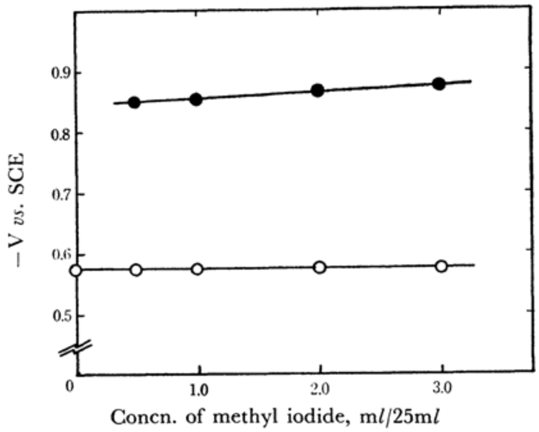


Fig. 9. The relation between concentration of methyl iodide and peak potential.
○: first peak, ●: second peak
The experimental conditions in Fig. 9 were the same as those in the case of Fig. 4.

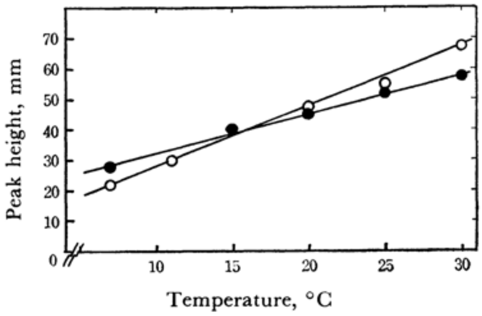


Fig. 10. The effect of temperature.
○: first peak, ●: second peak
The experimental conditions in Fig. 10 were the same as those in the case of Fig. 4.

The Effect of Dissolved Oxygen. The wave of dissolved oxygen overlaps with the wave of free sulfur in a mixed solution of 2 vol% of glacial acetic acid, 8 vol% of methyl iodide, 1.5 M of sodium acetate, and 90 vol% of methanol on s.w. polarograms. Therefore, it is necessary, for the determination of free sulfur, to remove the dissolved oxygen by passing nitrogen through for 3 min (see Fig. 11).

The results obtained by the proposed procedure are shown in Table 1.

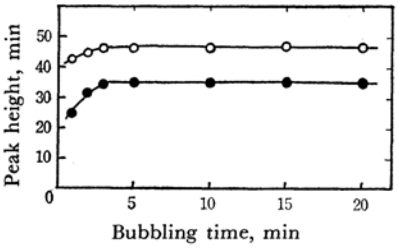


Fig. 11. The effect of dissolved oxygen.
○: first peak, ●: second peak
The experimental conditions in Fig. 11 were the same as those in the case of Fig. 4.

TABLE 1. RELATIVE ERROR IN THE DETERMINATION OF FREE SULFUR

Concn. ppm	Percentage error %
0.001	7.2
0.012	4.8
0.050	2.9
0.100	1.4

Summary

A s.w. polarographic method for the determination of a small amount of free sulfur in liquefied petroleum gases has been developed. This method seems to be the most useful method available for free sulfur determination.

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