S.W. Polarographic Determination of Mercaptan Compounds and Free Sulfur in Petroleum Naphtha

By

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Introduction

The application of a square-wave polarograph to the determination of small amounts of mercaptan compound and free sulfur in the mixed solution of methanol, pyridine and sodium acetate was studied. Mercaptan compounds and free sulfur in concentrations below 10 ppm were easily determined in these mixed solvent with a saturated calomel electrode. The derivative wave heights were proportional to the concentrations as predicted by the theory of S.W. polarography (1), (2). The polarographic waves of free sulfur consisted of two waves; peak potential for the 1st wave was -0.52 V. *vs.* SCE. The peak potential of 2nd wave was -0.72 V. *vs.* SCE. The peak potential of mercaptan compound (*n*-propylmercaptan) was -0.50 V. *vs.* SCE.

The decomposition of mercaptan compounds in 0.4 M sodium acetate at room temperature could be neglected within about an hour. The presence of disulfide had no influences on both the peak potential and the wave height. Hydrogen sulfide was removed by precipitation with cadmium sulfate. The limit of determination was governed by the solubility of naphtha in the base solution. The optimum region was in the concentrations from a few to 0.001 weight %. The procedure was that the sample was dissolved in the mixed solution of 14 vol. % of pyridine, 86 vol. % of methanol, 0.4 M sodium acetate and the solution was polarographed. The time required was only 30 minutes.

The method has the higher sensitivity than the conventional polarography, and was affected by irreversibly reduced materials, such as oxygen, on the measurement of mercaptan and free sulfur.

Attempts to increase the sensitivity of polarographic determination of these trace components were made in this paper.

Apparatus and Reagents

The Yanagimoto Model PA-102 recording polarograph and PM-1 multiplier attachment were used. The polarographic H-type cell with a saturated calomel electrode was used. A large capacitor (2000 μ F. electrolytic) was connected between the SCE and a platinum electrode to minimize resistance effects (See Fig. 1).⁽³⁾ The capillary constants in an open circuit ($h=61.0$ cm) were

$$t=3.8 \text{ seconds}$$

$$m=2.721 \text{ mg. per second}$$

All experimental measurements were made in an air-conditioned room with the temperature held constant to $25^{\circ}\pm 0.1^{\circ}\text{C}$. Fifty-milliliter flasks were used to dilute the sample

Fig. 1. H-cell with dropping-mercury cathode.

with the mixed solution of electrolyte-solvent.

Wako's methanol, pyridine and sodium acetate were used. All of the reagents and chemicals used were of commercial extra pure grade or analytical reagent grade, and their purities were examined beforehand by polarography. Powdered monoclinic sulfur (free sulfur) of better than 99.9% purity was used for the preparation of standard solutions. The mixed solution of electrolyte-solvent was prepared by mixing 86 vol. % of methanol, 14 vol. % of pyridine and 0.4M sodium acetate.

A standard solution of known sulfur content was prepared by dissolving weighed amounts of the monoclinic sulfur in the solvent. The monoclinic form of sulfur was used because it was more soluble than other forms of sulfur, and also because the monoclinic form was used in doctor sweetening processes for gasolines.

Experimental

Because the method was to be applied mainly to petroleum samples, one of the major problems was to find a satisfactory solvent for the gasoline, sulfur, mercaptan and a supporting electrolyte. At first, the mixtures of pyridine, benzene, methanol and sodium acetate in various proportion were tried, but were found unsatisfactory mainly because gasoline would not blend enough with the mixed of electrolyte-solvent to permit an accurate determination of sulfur in the concentration range of 1 to 3 ppm in the gasoline; at least that 10 ml. of the gasoline sample blends in 50 ml. was necessary for the most accurate work in this concentration range. Mixtures of various amounts of the low molecular weight alcohol with pyridine and sodium acetate were investigated as electrolyte-solvent, and the most suitable combination found for mixing with gasoline was the mixture of methanol, pyridine and sodium acetate. The methanol serves as a solvent for gasoline; the pyridine serves as a solvent for free sulfur and mercaptan compounds.

Polarogram of mercaptan compound and free sulfur

(1) Mercaptan compound.

Mercaptan compounds were used ethyl-, *n,t*-propyl-, *n,i,t*-butyl-, *n,i*-amyl-, *n,t*-octyl-, lauryl, phenyl-, benzylmercaptan, and so on. Their purity was examined beforehand polarographically. Peak potential of their compounds covered -0.48 to -0.55 V. *vs.* SCE. S.W. polarogram of 20 ppm *n*-propyl mercaptan in the solution of 14 vol. % of pyridine, 86 vol. % of methanol and 0.4M sodium acetate is given in Fig. 2.

(2) Free sulfur.

The polarographic wave of free sulfur consisted of two waves; peak potential for the 1st wave was -0.52 V. *vs.* SCE. The peak potential of the 2nd wave was -0.72 V. *vs.* SCE (See Fig. 2).

The 1st wave of free sulfur and wave of mercaptan showed the same peak potential. Therefore, when free sulfur exists with mercaptan compound, the true wave height of mercaptan is obtained by deducting that of the 1st wave of free sulfur from the total wave height.

Fig. 2. Polarographic wave of mercaptan and free sulfur in methanol, pyridine and sodium acetate.

(1) 20 ppm. *n*-Propyl mercaptan, (2) 4 ppm. Free sulfur, (3) (1)+(2), Initial Volt. -0.3 V. vs. SCE.

Parallel Capacitance : $50 \mu\text{F}$. Recorder Sens. : $0.02 \mu\text{A}/\text{mm}$. Amplifier Sens. : $1/200$, Gate : 1-7, S.W. Volt. Adjust : 20, Time constant : 81.

Fig. 3. Effect of temperature on the polarogram of mercaptan.

Sample : 20 ppm. *n*-Propyl mercaptan. Initial Volt. -0.3 V. vs. SCE.

Parallel Capacitance : $50 \mu\text{F}$. Gate : 1-7, S.W. Volt. Adjust : 20, Time Constant : 81.

The Effect of dissolved oxygen

The wave of dissolved oxygen is overlapped by the wave of free sulfur and mercaptan in the mixed solution of 14 vol. % of pyridine, 86 vol. % of methanol, $0.4 M$ sodium acetate on S. W. polarograms. Therefore, it is necessary for the determination of free sulfur and mercaptan to remove the dissolved oxygen by passing nitrogen for 30 min.

The Effect of temperature

(1) Mercaptan compound.

At low temperature (10°C) the asymmetrical form of the S.W. ad-

sorption wave is observed, but the wave form is being practically symmetrical as the temperature is raised (See Fig. 3). In the case of drawing method A, the plot of wave height against temperature shows no change, but in the case of drawing method B, it yields a straight line as shown in Fig. 4. It is seen in Fig. 4 that the wave height at any temperature is almost independent of the direction in which the temperature is changed. The temperature coefficient is about 19.6% per degree in the neighbourhood of 25°C.

Fig. 4. Effect of Temperature (Mercaptan).

Parallel Capacitance : 50 μ F. Recorder Sens. : 0.02 μ A/mm. Amplifier Sens. : 1/100, Gate : 1-7, S.W. Volt. Adjust : 20, Time Constant : 81, Sample : 20 ppm *n*-Propyl mercaptan

Fig. 5. Effect of Temperature (Free Sulfur)

Parallel Capacitance : 50 μ F. Recorder Sens. : 0.04 μ A/mm. Amplifier Sens. : 1/100, Gate : 1-7, S. W. Volt. Adjust : 20, Time Constant : 81.

Fig. 6. Calibration curve of Mercaptan.
Parallel Capacitance : 50 μ F. Gate : 1-7, S.W. Volt.
Adjust : 20, Time Constant : 81.

Fig. 7. Calibration curve of Free sulfur.
Parallel Capacitance : 50 μ F. Gate : 1-7
S.W. Volt. Adjust : 20, Time Constant : 81.

(2) Free sulfur.

The polarographic wave of free sulfur consisted of two waves; the wave height for the 1st wave was not affected by temperature, but the 2nd wave increases as the temperature is raised. A plot of wave height against temperature yields a curved line as shown in Fig. 5.

Calibration curve

(1) Mercaptan compound.

A known amount of the standard solution of mercaptan (*n*-propyl mercaptan) was added to the mixture of 14 vol. % of pyridine and 86 vol. % of methanol in a 50 ml. volumetric flask. An aliquot of the solution was taken in a cell and polarographed after deaeration. A calibration curve obtained by these procedures

is shown in Fig. 6. The poor linearity of calibration curve may be due to the nonlinearity of rectifier equipped in the instrument. The detectable limit of concentration of mercaptan compound was about 1 ppm.

(2) Free sulfur.

The procedures of those experiments are the same as those in case of the mercaptan compound (See Fig. 7). The detectable limit of concentration of free sulfur was about 1 ppm.

Conclusion

In case of mercaptan the applied potential of -0.52 V. *vs.* SCE was used to measure the wave height. The results are shown in Table 1. It was observed that a well-defined wave was obtained only when the concentration of mercaptan was higher than 1 ppm and that the wave was rather drawn out, extending from about -0.25 to -1.0 V. *vs.* SCE. A typical polarogram is shown in Fig. 2.

In case of free sulfur, the applied potential at -0.72 V. *vs.* SCE was used to measure the wave height.

Table 1

Mercaptan (<i>n</i> -Propylmercaptan)		Free Sulfur	
Concentration (ppm)	Percentage error (%)	Concentration (ppm)	Percentage error (%)
20	7.0	10	1.2
5	9.6	6	3.0
1	10.3	1	4.0

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ク形波ポーログラフ法による石油留分中の微量メルカプタン化合物および遊離イオウの同時定量

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本分析法はク形波ポーログラフ法によりナフサ留分中の極微量メルカプタンおよび遊離イオウを同時定量することを目的とする。メルカプタンのポーログラフ法による定量法は1958年のハンブルスキム法による定性的な検討以外、今までのところほとんど行なわ

れていない。また現在の ASTM 法、その他の方法では、とうていこのような物質の極微量(数 ppm)分析は不可能である。一方、石油留分中の遊離イオウの定量法については、1950年に Hall が、ガソリン留分にポーログラフ法を適用して以来、現在までに数種の

改良法が発表されている。

(1) 装置：柳本製、交直両用ポーラログラフ PA102 型および高感度装置 PM 1 型を使用した。電解セルには Fig. 1 に示すごとく H 型セルに 2000 μ F コンデンサーを接続し、液絡部の抵抗を出来るだけ小さくして実験を行なった。

(2) 基礎液：最適条件としてピリジン、メタノール、酢酸ナトリウムの混合溶液を得た。そこで試料の溶解度、誘電率、その他種々条件を考慮して、その割合を検討した結果、ピリジン 14 vol%，メタノール 86 vol%，0.4M 酢酸ナトリウムが最適と認めた。

(3) ポーラログラム：メルカプタンについては十数種類の化合物について検討した結果、本分析法の基礎液によると、頂点電位は $-0.48 \sim -0.55$ V. vs. SCE を示すことがわかった。その一例として、20 ppm. の *n*-Propyl mercaptan が本基礎液中であたえるポーラログラムを Fig. 2 に示す。遊離イオウは、二段波を示し、第 1 波は -0.52 V, 第 2 波は -0.72 V. vs. SCE に頂点電位を示す。しかるに、遊離イオウの第 1 波とメルカプタン化合物の波が重なってくる。故に定量時において、遊離イオウが共存している場合には、遊離イオウの第 2 波の波高から検量線により第 1 波の波高を求め、メルカプタンの真の波高を求めねばならない。

(4) 温度の影響：メルカプタン化合物については、

Fig. 3 に示す如く、温度変化によって、ポーラログラムは変化する。この現象は滴水銀電極上での吸着現象によるものではないかと考えられる。波高は作図の仕方によって異なるが、Fig. 3 の (A) 法によると波高に変化なく、(B) 法によれば温度に比例して波高は高くなる。(Fig. 4 参照) この場合の温度係数は 19.6% /degree であった。また遊離イオウについて、10~35 °C の範囲内で検討した結果、Fig. 5 に示すごとく、第 1 波は温度の影響を受けないが、第 2 波は温度上昇とともに波高は増加する。

(5) 共存物質の影響：ナフサ留分中で遊離イオウとメルカプタン以外のイオウ化合物として一応沸点範囲から考えて、 H_2S , Disulfide などが考えられる。このうち H_2S は -0.67 V. vs. SCE にポーラログラムを示し、遊離イオウのポーラログラムに影響をおよぼす。したがって、 H_2S は硫酸カドミウム処理により除去する。次に Disulfide であるが、これは本条件においてポーラログラムを示さない。

以上の各条件により、分析した結果、分析精度は Table 1 に示したとおりとなり、定量下限は、おのおの 1 ppm で、この時の相対誤差はメルカプタンについては 10.3%，遊離イオウは 4.0% となる。

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