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The Spectrophotometric Determination of Thiophene in Petroleum Naphtha with α-Nitroso-β-naphthol

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A colorimetric method for the direct estimation of thiophene in petroleum naphtha without interference from the other sulfur compounds present has been worked out. The test is based on the blue-green color produced by the reaction between thiophene and α-nitroso-β-naphthol in the presence of sulfuric acid. The procedure accounted for from 10.0 mg./ml. of thiophene sulfur down to a mere trace of thiophene, of the order of 0.01 mg./ml. thiophene sulfur.

In the preceding paper[1] we have reported a s. w. polarographic determination of mercaptan compounds and free sulfur in petroleum naphtha. This paper will describe an investigation of α-nitroso-β-naphthol as a colorimetric reagent in concentrated sulfuric acid for the determination of thiophene. A survey of the literature revealed that α-nitroso-β-naphthol has not been reported on previously for the colorimetric determination of thiophene. The absorption curves of the reaction products are given in the visible region. Isosbestic absorption occurs at 640 mμ, where Beer's law is obeyed, and the color is stable for at least 4 hr. Thiophene can be determined in petroleum naphtha at concentrations as low as 0.01 mg. per ml., with a percentage error of 16.0%.

The effects on the absorbance of a reagent solution by many of the more common sulfur compounds were studied; the following compounds did not interefere at the concentrations tested: elemental sulfur (1.0 mg./ml.), di-*n*-butyldisulfide (1.0 mg./ml.), di-*n*-butylmercaptan (1.0 mg./ml.), and di-*n* butyltrisulfide (1.0 mg./ml.).

The reagent, which consists of α-nitroso-β-naphthol dissolved in concentrated sulfuric acid, reacts quantitatively with thiophene compounds, producing a stable blue-green color. The color formation, like that of the Indofenin reaction,[2-4] is believed to be due to the formation of dehydrocondensation compounds by the concentrated sulfuric acid in the reaction mixture.

Experimental

Reagents.—A thiophene (Tokyo Kasei Organic Chemicals) stock solution was prepared by dissolving thiophene of an analytical grade in petroleum naphtha free from sulfur compounds. It was then diluted with that same petroleum naphtha to a desired concentration. An α-nitroso-β-naphthol (Wako Chemicals) was dissolved in concentrated sulfuric acid (Ishizu Chemicals) to give a concentration of 5×10^{-5} mol./l.

Apparatus. — Spectrophotometric measurements were made with a Shimazu, model SV-50A, spectrophotometer, using 5 cm. transmission cells. All experiments were carried out at 25±0.5°C.

Procedure.—Pipet 2.5 ml. of 1×10^{-3}M α-nitroso-β-naphtohol solution and 10 ml. of the sample solution into a 100 ml. separatory funnel. Stopper the funnel and shake vigorously for at least 60 sec. Allow the two phases to separate, and draw off the lower sulfuric acid layer into a clean, dry, 50 ml. volumetric flask. Add 10 ml. of sulfuric acid, stopper the funnel, and shake for 30±5 sec. Again allow the layers to separate. Draw off the lower layer and combine it with the first extract in the 50 ml. volumetric flask. Dilute to volume with sulfuric acid and mix well.

Read the absorbance at 640 mμ, using a 5-cm. cell and using the reagent blank as the reference material.

Results and Discussion

The intensity and stability of the colored complex formed are not influenced by the temperature

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

[2] G. Heller, *Angew. Chem.*, **37**, 1017 (1924).

[3] G. Heller, *Chem. Ztg.*, **54**, 585 (1930); **57**, 74 (1933).

[4] W. Steinkopf et al., *Ann.*, **541**, 238 (1939); **546**, 211 (1941).

of the solvents, the photochemical reaction, or the presence of impurities in the reaction mixture at 640 mμ. To illustrate the influence of each variable and to find the best conditions for obtaining reproducible results, each variable was considered separately.

Absorption Spectra.—The absorption spectrum of the reagent was studied from 380 to 720 mμ. The absorbance was negligible above 380 mμ, but it showed a steady increase at lower wavelengths without reaching a maximum. The absorption spectrum of the complex was studied from 380 to 720 mμ. No study was made below 380 mμ because of the high absorbance of the reagent in this range. Two absorption maxima occur in the spectrum of the complex between 380 and 720 mμ. The working portion of the curve is shown in Fig. 1. All the absorbance measurements for this investigation were made at 640 mμ in order to minimize the interfering absorbance of the α-nitroso-β-naphthol - thiophene complex, which is lower at this wavelength than at 430 mμ.

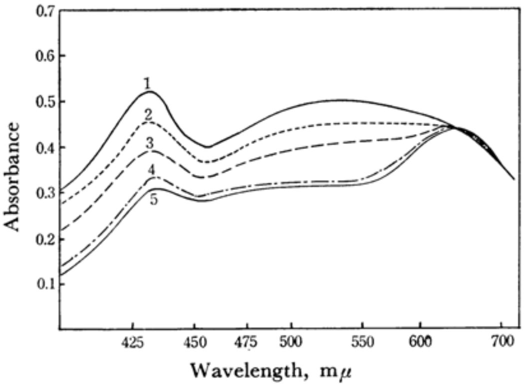

Fig. 1. Absorption spectrum of the reaction product of thiophene and α-nitroso-β-naphthol, and the effect of time.
1: 25 min. 2: 45 min. 3: 90 min. 4: 150 min. 5: 180 min. Thiophen: 0.85 mg./ml.

The Effect of Reagent Concentration.—In order to study the effect of the concentration of α-nitroso-β-naphthol, a series of absorbances was measured at various concentrations of α-nitroso-β-naphthol, using standard petroleum naphtha and reagent blanks of the same concentration as points of reference. Figure 2 gives the effect of the concentration of α-nitroso-β-naphthol in the reaction mixture on the absorbance of solution. It is apparent that a concentration of 5×10^{-5} mol./l. α-nitroso-β-naphthol is necessary in order to obtain a maximum color with this reaction. The absorbance at the isosbestic point of 640 mμ is affected by the amount of α-nitroso-β-naphthol below 5×10^{-5} mol./l. In the thiophene determination, therefore, a 5×10^{-5} mol./l. reagent solution was used, and the absorbance

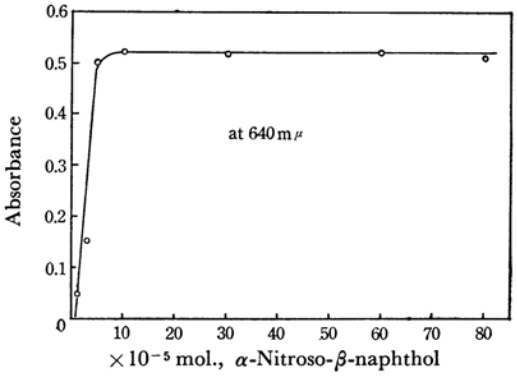

Fig. 2. The effect of addition of α-nitroso-β-naphthol. Thiophene: 1.0 mg./ml.

measurements were made at 640 mμ.

Shaking.—The maximum absorptivity was obtained when the α-nitroso-β-naphthol - concentrated sulfuric acid and petroleum naphtha (sample) were shaken vigorously for at least 60 sec. Procedure is recommended in order to minimize any variations resulting from differences in the rate of shaking.

The Effect of the Temperature on Color Formation.—The absorbance of the solution of the α-nitroso-β-naphthol - thiophene complex at 430 mμ gradually decreased with the time of standing at 10 to 35°C. About 15% of its intensity diminished within the first 2 hr., then it remained constant for an additional 2 hr. However, the absorbance at the isosbestic point (see Fig. 1) of 640 mμ remained constant for several hours (see Fig. 3).

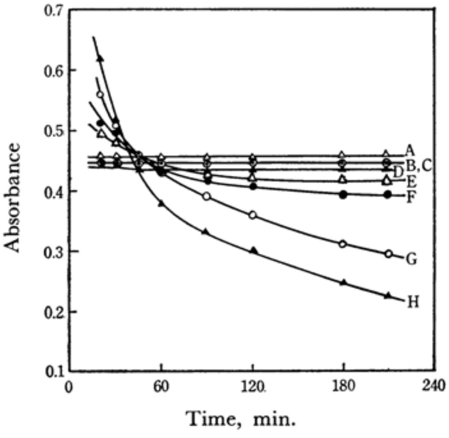

Fig. 3. Effect of temperature and time on color development.
A, B, C, D: 640 mμ, E, F, G, H: 430 mμ
△: 10°C, ●: 15°C, ○: 25°C, ▲: 35°C
Thiophene: 0.85 mg./ml.

The Effect of the Photochemical Reaction.—The authors have found that ordinary room light (from 100 W. tungsten bulbs) catalyzes the undesired reaction. Fig. 4 shows that the spectrum of the α-nitroso-β-naphthol - thiophene complex is stable if the solutions are kept in the dark or are exposed to light at 640 mμ, but that a change occurs at 430 mμ. The authors find that the absorbance at 430 mμ decreased appreciably in a few minutes if exposed to light, but it decreased much more slowly if kept in the dark.

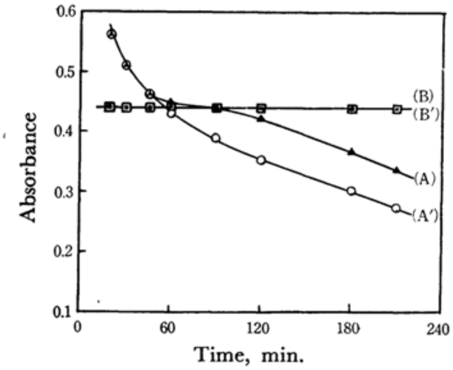

Fig. 4. Effect of light on spectra of α-nitroso-β-naphthol - thiophene complex.
Thiophen: 0.85 mg./ml.
(A): in Dark, (A′): in Light } 430 mμ, (B): in Dark, (B′): in Light } 640 mμ

Conformity to Beer's Law.—Measurements of the absorbance were made with a number of colored solutions containing varying amounts of thiophene. The straight-line calibration curve (see Fig. 5) showed a conformity to Beer's law for the concentration range studied. The useful range for a 5 cm. cell is 0.01 to 0.12 mg. per ml.

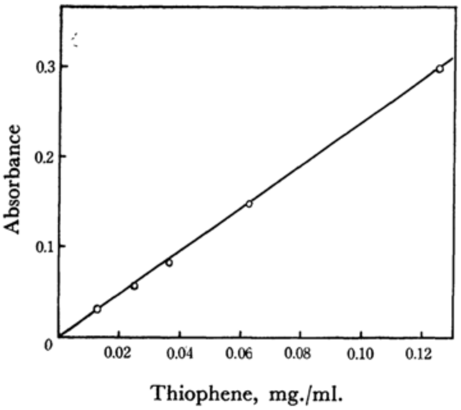

Fig. 5. Calibration curve.

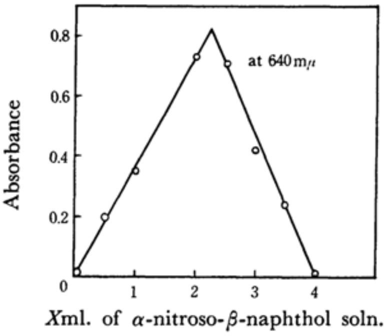

Fig. 6. Continuous variation method.
Continuous variation method applied to α-nitroso-β-naphthol - thiophene complex, Xml. of reagent added to 4−Xml. of thiophen solution.

The Determination of the Formula of the Complex.—The methods of continuous variation[5] were employed in order to determine spectrophotometrically the reagent-to-thiophene ratio of the complex. The continuous-variations method was performed by mixing 4−X ml. of a 0.01 M solution of α-nitroso-β-naphthol and X ml. of a thiophene solution of the same concentration. Absorbance measurements were made at 640 mμ for the eight solutions. The continuous-variation plot using corrected absorbance values is shown in Fig. 6. The maximum absorbance occured at about a 0.5 mol. fraction of thiophene, indicating that one mole of α-nitroso-β-naphthol coordinated with one mole of thiophene.

Relative Error in the Determination of Thiophene.—The method seems to be the most favorable one for thiophene determination. The results obtained by the proposed procedure are shown in Table I.

TABLE I. RELATIVE ERROR IN THE DETERMINATION OF THIOPHENE

Concn. mg./ml.	Percentage error %
0.01	16.0
0.02	10.5
0.03_8	5.0

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[5] J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).