Identification of 3-Methylthiophene in Wilmington, California, Crude Oil

C. J. THOMPSON, H. J. COLEMAN, C. C. WARD, and H. T. RALL
Petroleum Experiment Station, Bureau of Mines, U. S. Department of the Interior, Bartlesville, Okla.

The presence of thiophene and 2-methylthiophene in Wilmington, Calif., crude oil was recently reported (*2*); 3-methylthiophene also was suspected to be present but could not be identified with certainty. Figure 1 outlines preparation of a sulfur concentrate, in which 3-methylthiophene was identified, from the 38° to 111° C. boiling-range distillate of Wilmington crude oil. All percentages shown are weight-per cents based on total crude oil. By successive percolations of the 38° to 111° C. concentrate through alumina, a sulfur concentrate representing 0.008% of the crude oil was obtained. While the sulfur content of the final concentrate was only slightly in excess of 1%, this represented more than a 100-fold increase in the sulfur content of the original distillate. The remainder of the concentrate consisted largely of toluene and benzene, with minor percentages of pentane, chloroform, and carbon tetrachloride, solvents used in preparing the concentrate and not eliminated in the processing. Possibly, extremely small percentages of sulfur compounds other than thiophene and its two methyl derivatives also were present, but no traces of these were found. The reason for suspecting that such compounds are present is that it is difficult to believe that they are wholly absent in any crude oil. This question is being investigated further.

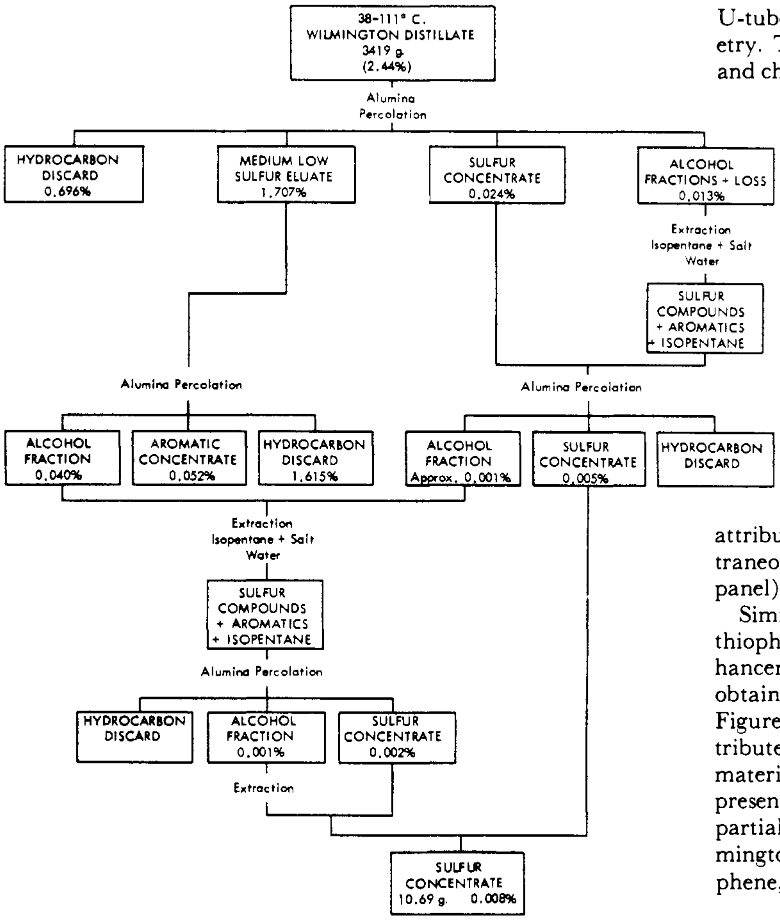

Figure 1. Summary of the processing of a 38° to 111° C. boiling-range distillate from Wilmington crude oil.

The gas-chromatographic column used in the identification work was a 1/4-inch-diameter by 6-foot-long copper tube filled with 40 to 50 mesh, acid-washed firebrick treated with 20 grams of Dow Corning silicone oil per 100 grams of firebrick. The operating temperature was 38° C.; a carrier gas (helium) flow rate of 100 ml. per minute was used. The sensing element was a thermistor type used in a conventional bridge circuit. The sample introduction system was that described by Tenney and Harris (*1*), which is now available in commercial models. In this work a 0.02-ml. sample was used.

Figure 2 (top panel) shows the gas-liquid chromatogram obtained on the 38° to 111° C. sulfur concentrate (see Figure 1, last block). Peaks in the curve corresponding in emergence times to those of thiophene, 2-, and 3-methylthiophene, toluene, benzene, carbon tetrachloride, and chloroform were obtained and are evident in the figure. The material emerging from the column during the formation of the two small peaks labeled "carbon tetrachloride" and "chloroform" was trapped in glass U-tubes cooled with liquid air and identified by mass spectrometry. The addition of small amounts of carbon tetrachloride and chloroform to the sample enhanced the height of the peaks attributed to these compounds and did not produce any extraneous peaks in the chromatogram (see Figure 2, center panel).

Similarly, by adding small quantities of thiophene, 2-methylthiophene, and 3-methylthiophene to the original sample, enhancement of the peaks attributed to these compounds was obtained without extraneous peaks. These data are shown in Figure 2, top and bottom panels. Trapping of the peak attributed to 3-methylthiophene and examination of the trapped material by mass spectrometry gave additional evidence of the presence of this compound. The accompanying table shows the partial mass spectrum of the trapped GLC fraction from Wilmington concentrate compared to that of the 2-methylthiophene, 3-methylthiophene, and toluene:

	Relative Intensity			
m/e	Fraction	Toluene	2-Methylthiophene	3-Methylthiophene
91	100.0	100.0	. . .	. . .
92	72.7	72.0	. . .	. . .
97	100.0	. . .	100.0	100.0
98	52.4	. . .	53.5	53.0

In the small concentrations present, mass spectrometry was not able to distinguish positively between 2- and 3-methylthiophene, and it was necessary to resort to infrared spectrometry to establish these identifications. This was accomplished in the manner described below.

The sampling procedure for the preparation of an infrared sample employed a specially designed glass trap consisting of a small reservoir at the bottom, a coiled inlet tube to provide relatively large surface area for condensation, and a straight,

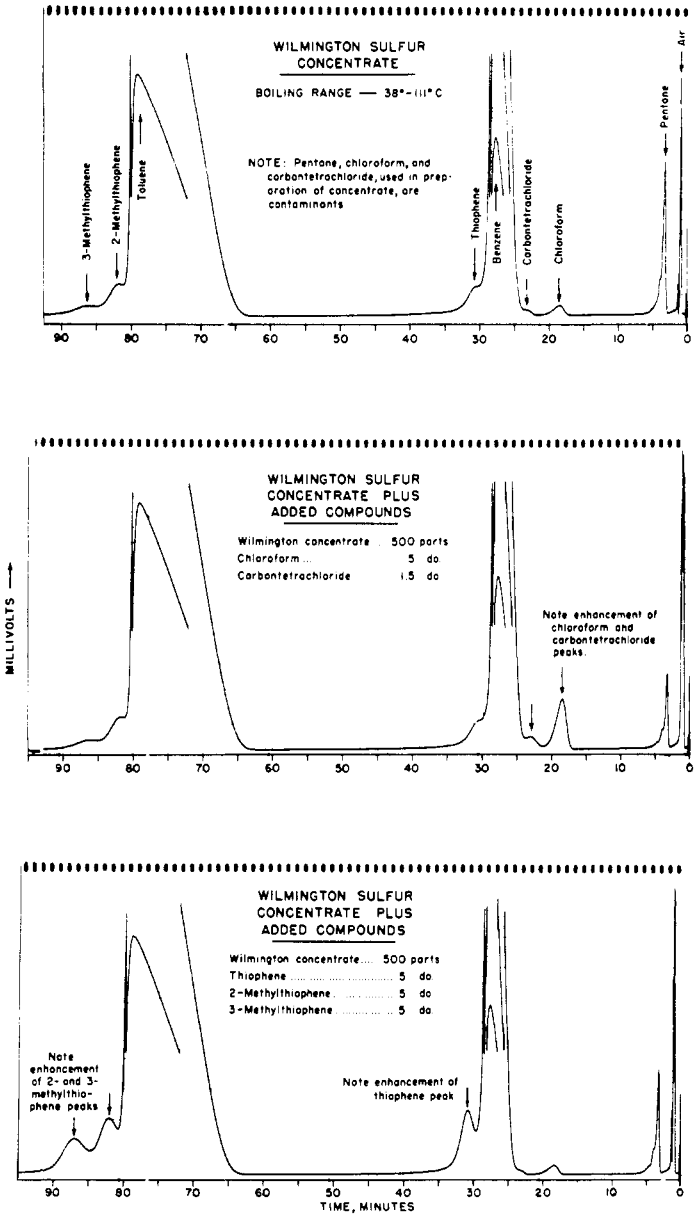

Figure 2. Gas-liquid chromatographic analysis of Wilmington 38° to 111° C. sulfur concentrate.

vertical tube on the outlet side to permit the withdrawal of sample from the bottom of the reservoir by means of a syringe and a long hypodermic needle. The trap was filled with helium, immersed in liquid air, and attached to the exit end of the gas chromatographic column for collection of sample which was begun on the trailing shoulder of the 2-methylthiophene peak. After the material forming the peak attributed to 3-methylthiophene had passed into the trap, the trap was disconnected. Because of the low concentration of 3-methylthiophene in the concentrate, the above trapping procedure was repeated in three additional chromatographic runs. The liquid-air cooled trap then was evacuated and raised from the coolant until only the reservoir remained immersed, and the upper portion of the trap warmed to effect a vapor transfer of the trapped material from the walls of the coiled tube to the reservoir. Helium then was admitted to the trap and 0.2 ml. of carbon disulfide added to dissolve the trapped 3-methylthiophene and produce a sample of sufficient size to fill an infrared cell.

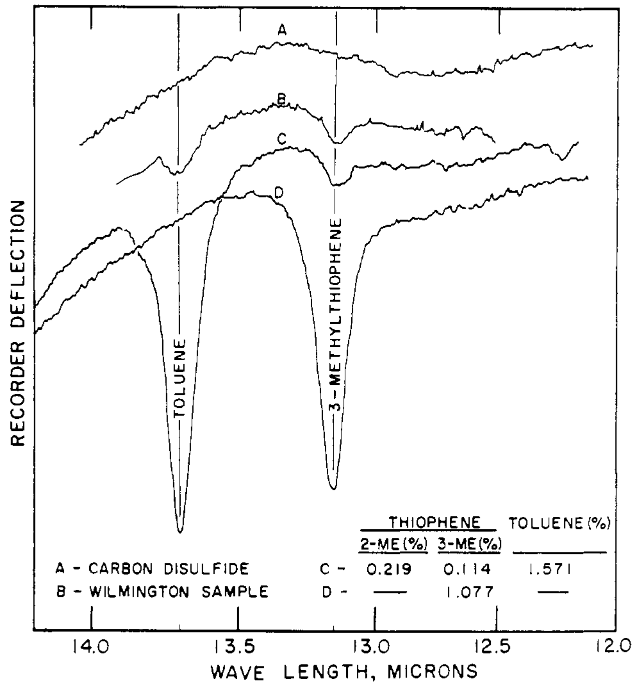

Figure 3. Absorption spectra of 3-methylthiophene fraction from C. gas-liquid chromatography of sulfur concentrate from Wilmington crude oil with comparison spectra.

Figure 3 shows the radiant energy transmitted through the cell and instrument path when the cell is filled with (A) carbon disulfide, (B) the collected sample diluted with 0.2 ml. of carbon disulfide, (C) a blend of toluene, 2-, and 3-methylthiophene in carbon disulfide, and (D) 3-methylthiophene in carbon disulfide. The strong absorption band of 3-methylthiophene at 13.16 microns is recognized immediately in the spectrum of the sample, as is the intense absorption band of toluene at 13.7 microns. 2-Methylthiophene is undoubtedly also present in the trapped sample, but its strong absorption bands at 11.78 and 12.24 microns are outside the wave length range used in scanning the Wilmington concentrate. Of the four probable components of the sample, carbon disulfide, toluene, 2- and 3-methylthiophene, the 13.16 microns absorption band is unequivocally that of 3-methylthiophene, and its presence in the sample spectrum is confirming evidence of the presence of this thiophene in Wilmington crude oil.

Because of the limited quantity of sulfur concentrate resulting from the processing of this low sulfur distillate it was considered impractical to expend any in the determination of total sulfur. However, a calculated value of slightly over 1% is in good agreement with the 1.0% value determined by GLC. This is to be expected because no evidence of sulfur compounds other than the three thiophenes could be found. The concentration of the 3-methylthiophene in the crude oil is not known with certainty, but it is estimated to be about 0.00006 weight %.

ACKNOWLEDGMENT

The authors acknowledge the assistance of Norman Foster and Pearl Tribble in obtaining the mass and infrared spectra used in the above investigation.

LITERATURE CITED

(1) Tenney, H. M., Harris, R. J., *Anal. Chem.* **29**, 316-7 (1957).
(2) Thompson, C. J., Coleman, H. J., Mikkelsen, Louis, Yee, Don, Ward, C. C., Rall, H. T., *Ibid.*, **28**, 1384-7 (1956).

RECEIVED for review November 7, 1958. Accepted February 2, 1959. 13th Southwest Regional Meeting, ACS, Tulsa, Okla., December 5-7, 1957. Investigation performed as part of the work of American Petroleum Institute Research Project 48A on "Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties," which the Bureau of Mines conducts at Bartlesville, Okla., and Laramie, Wyo.