Report of Investigations 4753

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United States Department of the Interior — November 1950

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UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
BUREAU OF MINES
James Boyd, Director

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ILLUSTRATIONS

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INTRODUCTION

One phase of the research and development work on synthetic liquid fuels conducted by the Bureau of Mines at Morgantown, W. Va. in cooperation with West Virginia University deals with the purification of synthesis gas.2/ Most of the experimental studies on gas purification have been directed toward the removal of organic sulfur from gas, either catalytically or by adsorption with activated carbon.3/

An important part of the purification program has been the development of suitable analytical methods for determining organic sulfur compounds. As the total sulfur content, organic and inorganic, of purified synthesis gas should not exceed 0.1 grain per 100 cubic feet, the need for accurate analytical methods is apparent. It is also apparent that such methods must be rapid if one wishes to evaluate various processes for removing sulfur from gas.

The organic sulfur found in most gas produced from coal is usually present as carbon disulfide, carbon oxysulfide, methyl and ethyl mercaptans, and thiophene. With the exception of thiophene, the remaining organic sulfur compounds respond similarly to catalytic treatment and can be removed effectively. Not only does thiophene resist most catalytic treatment, but it poisons some catalysts, rendering them ineffective in removing the other forms of organic sulfur.

Owing to this behavior of thiophene, it was decided to investigate analytical methods for determining this compound separately. In this laboratory, all other types of organic sulfur compounds are determined together and recorded as grains of sulfur as organic sulfur.

A review of the literature failed to disclose any convenient method for determining thiophene in gas, but many that could be used to determine thiophene in gasoline, benzene, etc. Of those methods presented in the literature for determining thiophene in liquids, the most satisfactory appeared to be that which employs the indophenine reaction. It was decided to study the efficacy of this method for determining thiophene in gas.

2/ Sands, A. E., Wainwright, H. W., and Schmidt, L. D., Purification of Synthesis Gas Produced from Pulverized Coal: Ind. Eng. Chem., vol. 40, 1948, pp. 607-620.

3/ Sands, A. E., Wainwright, H. W., and Egleson, G. C., Organic Sulfur in Synthesis Gas: Occurrence, Determination, and Removal: Rept. of Investigations 4699, 1950.

SUMMARY AND CONCLUSIONS

1. As little as 0.0001 grain of thiophene sulfur per 54.5 ml. of test solution can be detected.

2. The temperature at which the absorption of thiophene in the isatin-acid reagent is carried out affects the test and must be controlled. Calibration curves for temperatures ranging from 15° to 50° C. are presented.

3. The age of the isatin-acid reagent has a marked effect upon the intensity of color produced. In all tests the reagent is allowed to age 1 hour before it is used.

4. The presence of ferric sulfate as an oxidizing agent hastens the reaction, so that maximum color is obtained within 20 minutes.

5. Carbon disulfide and carbon oxysulfide do not interfere with the test; mercaptans do interfere and must be removed.

6. Unsaturated hydrocarbons interfere with the test, the degree of interference depending on the quantity and type of unsaturated hydrocarbon in the gas.

7. The intensity of color is measured with a spectrophotometer, using a wave length of 580 millimicrons.

8. A procedure for determining thiophene in a synthesis gas containing low amounts of unsaturated hydrocarbons is presented.

ACKNOWLEDGMENTS

The authors wish to express their appreciation to the entire personnel of the Gas Treating and Testing Unit whose cooperation in performing numerous tests was most helpful. Thanks also are extended to many students of West Virginia University who are employed by the Bureau of Mines as part-time workers.

DISCUSSION

Many investigators[4/], [5/], [6/] have determined specific organic sulfur compounds by using selective absorbing reagents. Recent work on the use of such selectivity is reported by Hakewill and Rueck.[7/] Their procedure calls

4/ Hutchinson, W. K., A Plant for the Removal of Sulfur Compounds by Oil Washing: Publication 175/64, Institution of Gas Engineers, 1937, p. 37.

5/ Riesz, C. H., and Wohlberg, C., Progress Report on Methods of Possible Utility for Determining Organic Sulfur Components in Gas: Proc. Amer. Gas Assoc., 1943, pp. 259-270.

6/ Kemper, W. A., and Guernsey, E. W., Organic Sulfur Compounds in Water Gas and Coke Oven Gas: Proc. Am. Gas Assoc., 1942, p. 364.

7/ Hakewill, H., and Rueck, E. M., Tentative Procedures for Determining Individual Organic Sulfur Compounds in Gas: Proc. Am. Gas Assoc., 1946, pp. 529-538.

for three separate runs: the first, in which total sulfur is determined by a combustion method; the second, in which residual sulfur is determined after mercaptans and hydrogen sulfide have been removed with cadmium chloride and thiophene has been removed with sulfuric acid; and the third, in which residual sulfur is determined after the above compounds have been scrubbed from the gas and the carbon disulfide and carbon oxysulfide have been removed with alcoholic potassium hydroxide. Values for the individual sulfur compounds can then be obtained by solving simultaneous equations. If one is interested only in the thiophene concentration, it is necessary to make only the first two runs.

This method was tried in this laboratory and, in addition to being long, gave erratic results, particularly with thiophene concentrations of less than 1 grain of sulfur per 100 cubic feet. This method, however, may be satisfactory when working with higher concentrations of thiophene.

For the determination of total sulfur, this laboratory uses the platinum spiral method developed by Lusby,8/ in which the organic sulfur is converted to hydrogen sulfide. Our modification of Lusby's method is described fully in a recent Report of Investigations.9/ The possibility of using the platinum spiral method with selective absorbing reagents for the determination of thiophene and other specific organic sulfur compounds has not been investigated, but such a procedure would reduce greatly the time necessary for a determination. As sulfuric acid absorbs both thiophene and mercaptans, a separate determination of mercaptans would be necessary. The method of Shaw10/ should be entirely suitable for such a determination.

Field and Oldach,11/ in their method for identifying organic sulfur compounds in concentrations of a few parts per million, rely on differences in solubility of the compounds in an inert solvent. Experimental data were obtained on carbon oxysulfide, methyl mercaptan, carbon disulfide, and various other compounds, but no mention is made of thiophene. They have evidently included this under higher-boiling compounds.

Soon after this laboratory began investigating the indophenine reaction for determining thiophene, Brady12/ published his method for determining thiophene, carbon oxysulfide, and carbon disulfide in producer gas. The method appears to be quite rapid and most promising. Brady claims that the minimal amount of sulfur that can be conveniently evaluated by this method is 0.013 grain per 100 cubic feet. Thiophene is scrubbed quantitatively from the gas with a piperidine-ethanol solution and is then determined spectrophotometrically.

Most of the work on the determination of thiophene described in the literature deals with the detection of thiophene in liquid hydrocarbons.

8/ Lusby, O. W., Quantitative Determination of Organic Sulfur: Proc. Am. Gas Assoc., 1936, pp. 752-754.

9/ See footnote 3.

10/ Shaw, J. A., Rapid Determination of Hydrogen Sulfide and Mercaptan Sulfur: Ind. Eng. Chem., anal. ed., vol. 12, 1940, pp. 668-671.

11/ Field, C., and Oldach, C. S., Identification of Sulfur Compounds in Gas Mixtures: Ind. Eng. Chem., anal. ed., vol. 18, 1946, pp. 669-672.

12/ Brady, L. J., Determination of Thiophene, Carbon Oxysulfide, and Carbon Disulfide in Producer Gas: Ind. Eng. Chem., anal. ed., vol. 20, 1948, pp. 512-514.

The widely used indophenine reaction appeared to be most sensitive, and it was decided to adapt this method for determining thiophene in gas.

The deep blue indophenine color that is formed by reacting thiophene with isatin appears to have been observed first by Baeyer.13/ Baeyer erroneously attributed the color to the presence of benzene, but Meyer,14/ in 1883, observed no blue color when experimenting with thiophene-free benzene. This led to Meyer's discovery of thiophene.

Schwalbe15/ first used the reaction as the basis of an analytical test for thiophene. Since 1915 there have been many modifications of the test, which are discussed in an excellent publication by French.16/

EXPERIMENTAL INVESTIGATIONS

Investigations at Morgantown for determining thiophene in gas were carried out with hydrogen as the carrier gas. A number of tests in which a gas mixture of approximately 50 percent hydrogen and 50 percent carbon monoxide was used as the carrier gas gave results that corroborated those obtained from the hydrogen tests. A typical analysis of this simulated synthesis gas follows:

	Percent
CO_2...	0.6
O_2....	.2
Ill...	.9
H_2....	49.7
CO....	44.2
CH_4...	.9
N_2....	3.5

During the investigation, it became evident that there were many variables that affect the isatin test and that must be controlled if accurate results are to be obtained.

Age of Isatin-Acid Solution

For the initial experiments, a stock solution of isatin, ferric sulfate, and sulfuric acid was prepared by adding concentrated sulfuric acid to an aqueous solution of isatin and ferric sulfate. 54.5 ml. of this solution was used for each test in preparing a calibration curve. During each determination the temperature of the isatin-acid solution was maintained at 25° C.

13/ Bayer, A., Research on the Indigo Blue Group: Ber., vol. 12, 1879, p. 1309-1320.

14/ Meyer, V., Benzene and Related Compounds in Coal Tar: Ber., vol. 16, 1883, pp. 1473-1478.

15/ Schwalbe, C., Study of the Thiophene Reaction of Liebermann: Ber., vol. 37, 1904, pp. 324-325.

16/ French, K. H. V., Colorimetric Determination of Less than 0.001 percent S as Thiophene in Pure Benzoles: Jour. Soc. Chem. Ind., vol. 65, 1946, pp. 15-23.

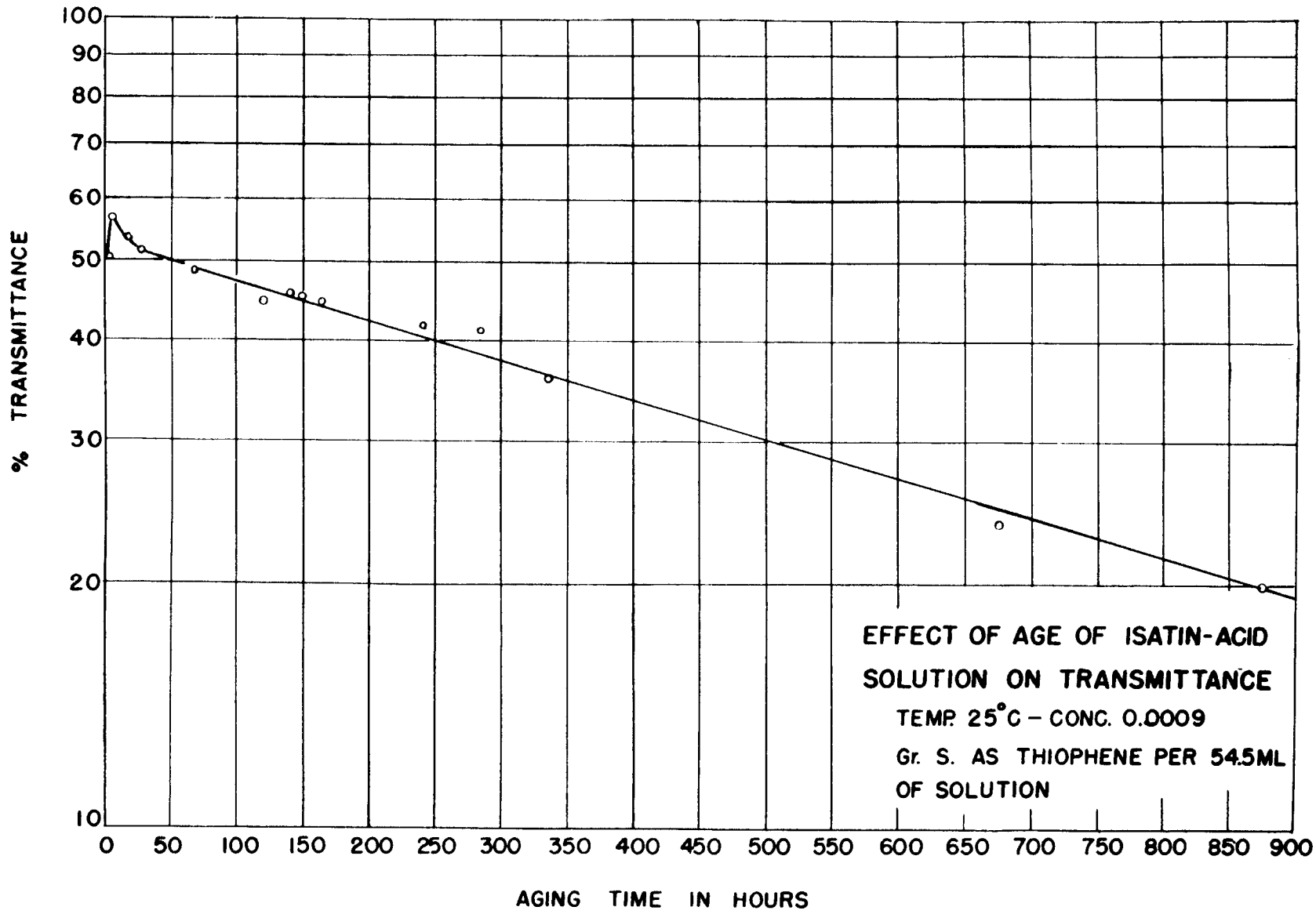

Figure 1. - Effect of age of isatin-acid solution.

Data from these first tests gave an excellent calibration curve. Tests conducted a week later gave points that also fell in a straight line, but these results were 10 percent higher than the originals. The same isatin-acid stock solution was used for both series of runs. A new batch of isatin-acid stock solution was prepared, and results from tests made with this freshly prepared solution closely approximated the original results. It was evident that the age of the solution affected the test, and a series of experiments were made over a period of 28 days to determine this effect precisely.

Figure 1 is a curve showing the effect of age of the isatin-acid solution upon the transmittance. It can be seen that during the first 5 hours after this solution has been prepared, there is a sharp increase in the percent transmittance, followed by a gradual and continual decrease.

It was apparent that the isatin-ferric sulfate solution and sulfuric acid could not be mixed and then used over long periods of time. The isatin-ferric sulfate solution and acid must be mixed prior to each determination and allowed to stand for a designated length of time. Our calibration curves were made by using isatin-acid mixtures that had aged for 1 hour.

Effect of an Oxidizing Agent

A review of the literature revealed that many investigators disagreed as to the importance of adding an oxidizing agent to the test solution.

Bauer[17] stated that the characteristic indophenine blue color does not form when pure sulfuric acid is used unless an oxidizing agent is present. Wray[18] confirmed this observation and suggested nitric acid as a suitable oxidizer. Lieberman and Pleus,[19] on the other hand, reported that no oxidizing agent is needed. French[20] found that a very small concentration of ferric sulfate was sufficient to cause an increase in the color developed after 1 minute. Further additions caused only slight improvement.

Experiments in this laboratory showed that the addition of ferric sulfate considerably reduced the time required to attain maximum color intensity. Those tests in which ferric sulfate was used gave maximum coloration within 20 minutes; those in which no ferric sulfate was used failed to reach the maximum within 2 hours after gas flow was stopped. This is illustrated by the following data, which were obtained from tests run simultaneously on gas having the same thiophene content.

17/ Bauer, F. W., Study of the Indophenine Reaction: Ber., vol. 37, 1904, pp. 1244-1245.

18/ Wray, C., The Indophenine Reaction: Jour. Soc. Chem. Ind., vol. 38, 1919, pp. 83-84. T

19/ Lieberman, C., and Pleus, B., The Thiophene Reaction with Nitrosylsulfuric Acid: Ber., vol. 37, 1904, pp. 2461-2464.

20/ See footnote 16.

Time, minutes	Transmittance, percent	
	With ferric sulfate	Without ferric sulfate
10	14.7	32.5
15	14.5	30.0
20	14.4	28.1
25	14.4	27.0
30	-	25.7
60	-	22.0
120	-	19.1

Additional data from tests that were not run simultaneously are summarized below. The concentration of thiophene in the gas was changed for each determination. It is interesting to note that there is no fading of the blue color in those samples that stood for 24 hours.

Time	Ferric sulfate added; transmittance, percent						
10 min.	25.2	38.1	9.97	50.4	16.1	5.68	5.80
15 min.	25.1	38.0	9.89	50.4	16.0	5.38	5.65
20 min.	25.0	38.0	9.90	50.3	16.0	5.28	5.42
25 min.	25.0	-	9.88	50.3	15.9	5.30	5.35
1 day	-	-	-	-	-	5.28	5.38

Time, minutes	Ferric sulfate not added; transmittance, percent		
10	21.9	38.5	61.0
15	20.4	33.3	56.9
20	19.1	32.1	55.4
25	18.2	30.6	53.3
30	17.4	29.8	52.1
60	15.1	25.7	50.6
120	13.0	23.2	48.0

Effect of Temperature

The temperature of the isatin-acid solution at the time of thiophene absorption has a pronounced effect upon the intensity of color produced. After the absorption phase of the test is completed, the temperature of the test solution is of no consequence.

Figure 2 presents a curve that shows the effect of temperature upon the transmittance of a sample containing 0.00135 grain of sulfur as thiophene. The maximum color is developed at 15° C.; lowering the temperature to 5° C. had no further effect. At temperatures higher than 15° C., there is a rapid decrease in color formation, resulting in a transmittance of 85 percent at 60° C. After a test had been made at 60° C. and the solution was cooled to room temperature, there was no increase in color intensity.

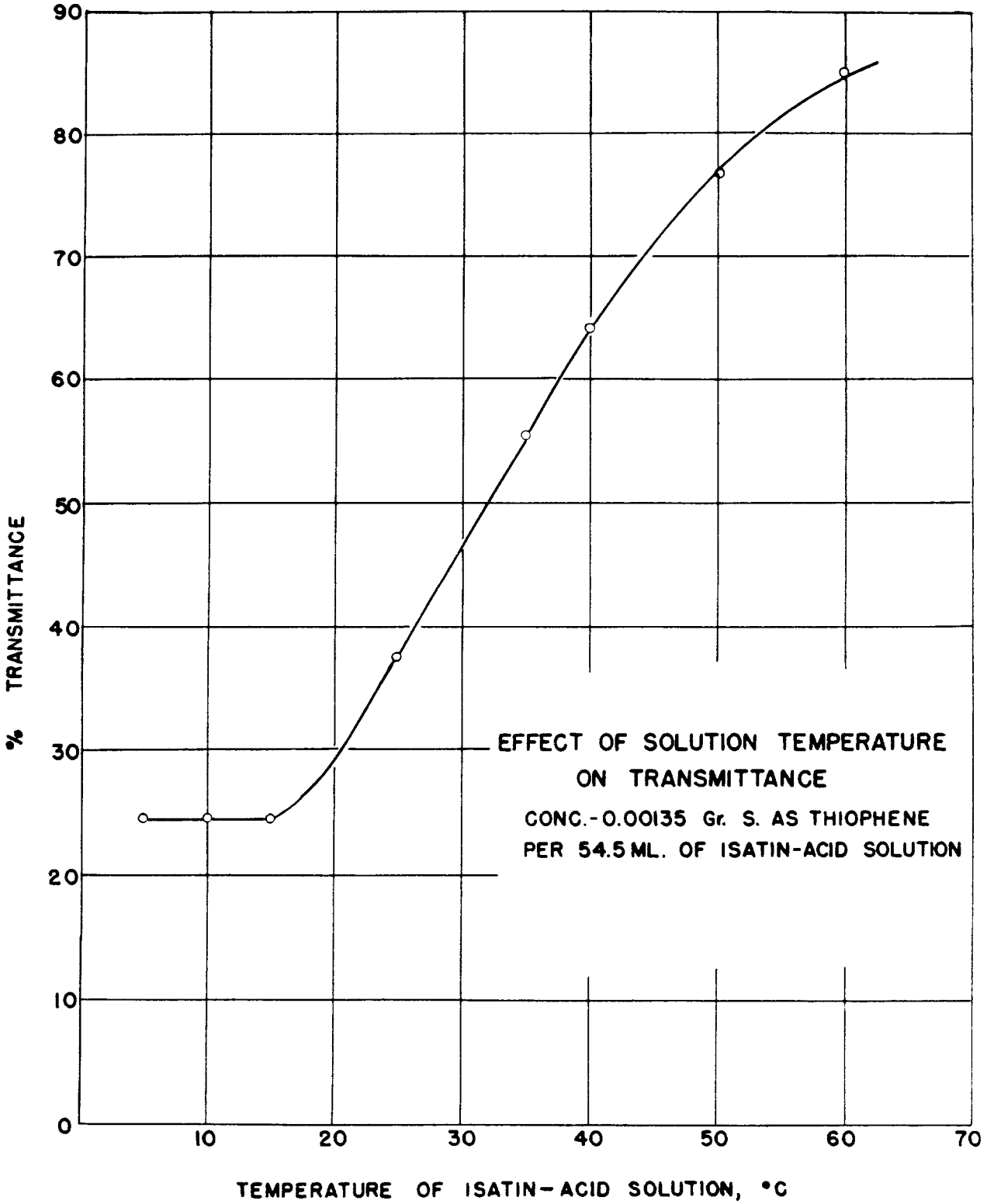

Figure 2. - Effect of solution temperature on transmittance.

It was thought that at the higher temperatures the absorption of thiophene was incomplete. However, a test was made in which the test solution, at 60° C., was followed by a second solution having a temperature of 25° C. The second solution gave a transmittance of 100 percent. This would indicate that at the higher temperatures the absorption of thiophene is complete but the reaction between the thiophene and isatin is not.

Interfering Substances

Carbon Disulfide

Tests were made on a simulated synthesis gas containing thiophene and carbon disulfide to determine whether the presence of the disulfide interfered with the isatin test. Data from these tests follow:

Gr. S as C_4H_4S	Gr. S as CS_2	Transmittance, percent
0.00145	-	34.0
.00145	0.01862	33.9
.00146	.00421	33.3
.00146	.00695	33.4

The sulfur values given in the table represent concentrations per 54.5 ml. of isatin-acid solution. The above data show that carbon disulfide, in concentrations at least 12 times greater than that of the thiophene, has no effect upon the test. The slight differences in the transmittance are within the accuracy of the test.

Ethyl Mercaptan

Similar tests were made in which ethyl mercaptan was added to the hydrogen-carbon monoxide gas mixture. Data for 54.5 ml. samples follow:

Gr. S as C_4H_4S	Gr. S as C_2H_5SH	Transmittance, percent
0.00135	-	38.4
.00135	0.00496	32.5
.00135	.00624	10.8
.00135	.00682	15.8
.00135	.00744	9.0
.00135	1/.0279	34.0
.00135	2/.00806	37.0

1/ C_2H_5SH removed from gas with one alkaline $CdCl_2$ scrubber.

2/ C_2H_5SH removed from gas with two alkaline $CdCl_2$ scrubbers.

The foregoing data show that ethyl mercaptan vitiates the isatin test by giving high results and must be removed.

The values for mercaptans in the last two determinations in the preceding table are those of the gas sample prior to scrubbing with an alkaline cadmium chloride solution. It can be noted that the resulting transmittances approximate rather closely that given for the solution in which no mercaptan was added to the gas, but there is an indication that some mercaptan may have passed through the scrubbers, as the transmittances are low.

Unsaturated Hydrocarbons

The first tests to study the effect of aliphatic unsaturated hydrocarbons were made by bubbling the carrier gas first through 100 percent amylene and then adding a known amount of thiophene. The characteristic blue color did not appear. Subsequent tests with ethylene and propylene gave similar results.

After reviewing the literature, it was concluded that this interference of unsaturated hydrocarbons was due to the alkylation of the thiophene in the α or the $\alpha\alpha'$ positions. Caesar[21] found that this reaction takes place readily in the presence of sulfuric acid at room temperature. Temperatures of 25° to 85° C. are preferred for the reaction of thiophene with reactive olefins, while temperatures of 75° to 150° C. are required for unreactive olefins. Such alkylation fills the positions on the thiophene ring, which are required for the isatin reaction as shown by Steinkopf.[22]

Numerous tests were run in an effort to selectively remove the unsaturated hydrocarbons from the gas. Laboratory investigations included oxidation with neutral and basic potassium permanganate and halogenation by using various bromine and iodine solutions. In all experiments, the thiophene was attacked along with the unsaturated compounds.

As attempts to remove unsaturated hydrocarbons selectively were unsuccessful, tests were run to determine the amount of these compounds that can be tolerated without invalidating the test.

Figures 3, 4, and 5 give curves showing the percentage of the thiophene in the gas that can be detected when the gas contains varying amounts of ethylene, butylene, and propylene. The concentration of the unsaturated hydrocarbon is given in percent by volume.

It can be noted from the curves that of the three compounds, ethylene contaminates the test to the greatest degree. This injurious effect may appear, at first, to be quite serious, but if the ethylene content is below 2 percent, reliable results can be obtained. With an ethylene concentration of 2 percent in the gas, approximately 85 percent of the thiophene can be detected. This, of course, involves an error of 15 percent, which is large as regards to percentage but is not too serious when dealing with extremely low concentrations of thiophene.

Two tests were made on gas containing ethylene and very low concentrations of thiophene. Results from these tests follow:

21/ Caesar, P. D., Alkylation of Thiophene with Olefins: Jour. Am. Chem. Soc., vol. 70, 1948, pp. 3623-3625.

22/ Steinkopf, W., The Chemistry of Thiophenes: T. Steinkopf, Dresden and Leipzig, 1941, p. 127.

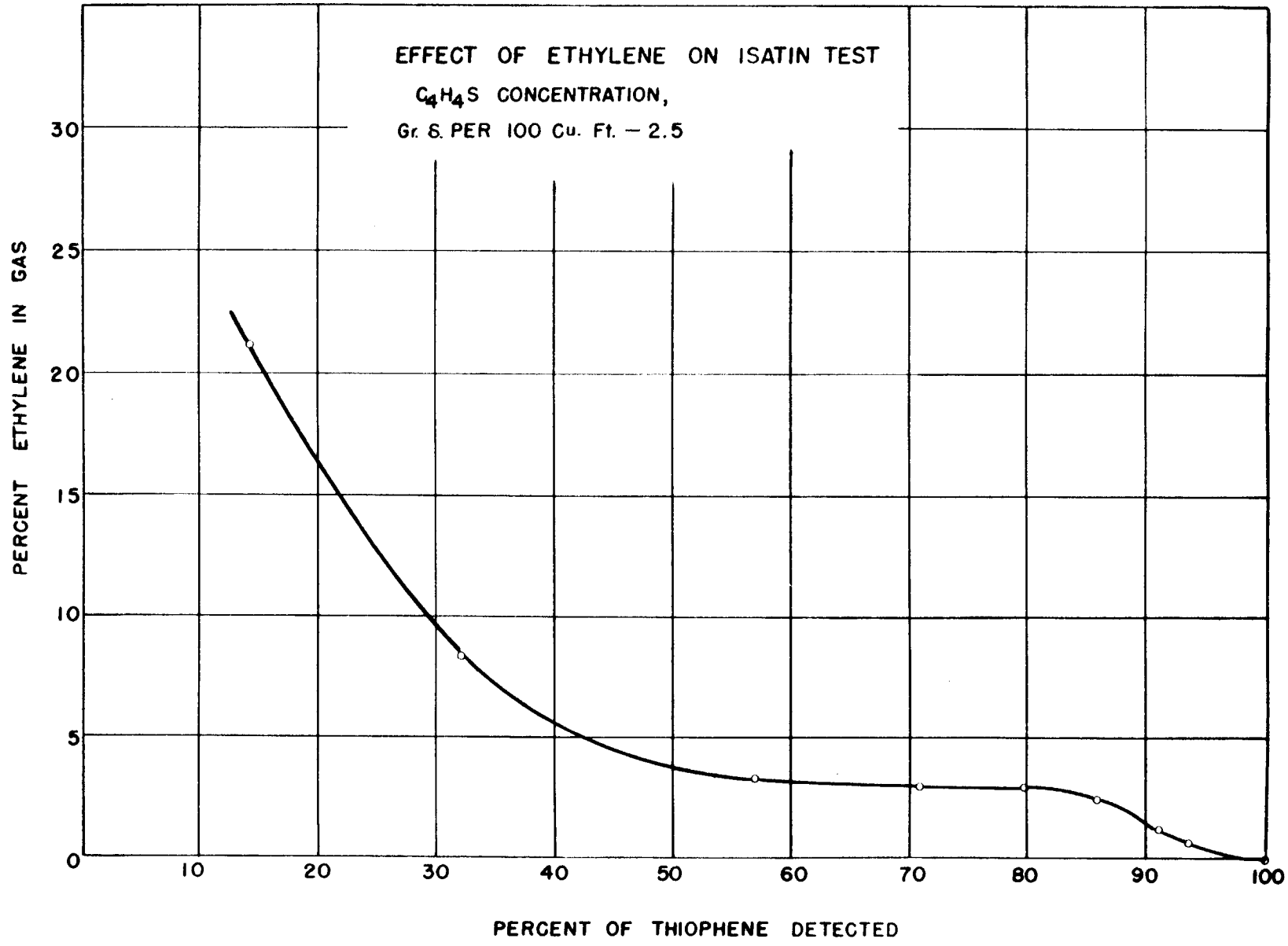

Figure 3. - Effect of ethylene on isatin test.

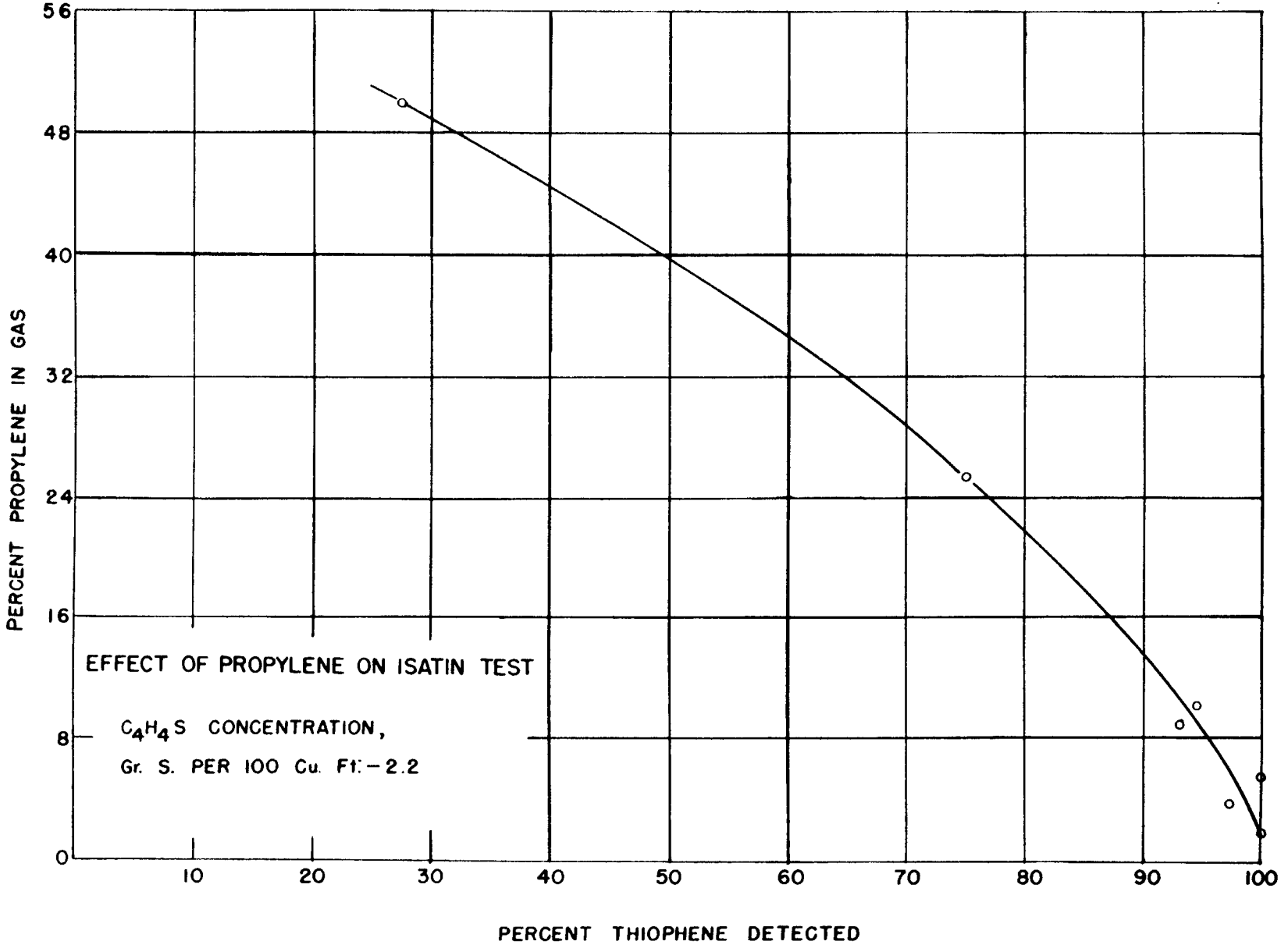

Figure 4. - Effect of propylene on isatin test.

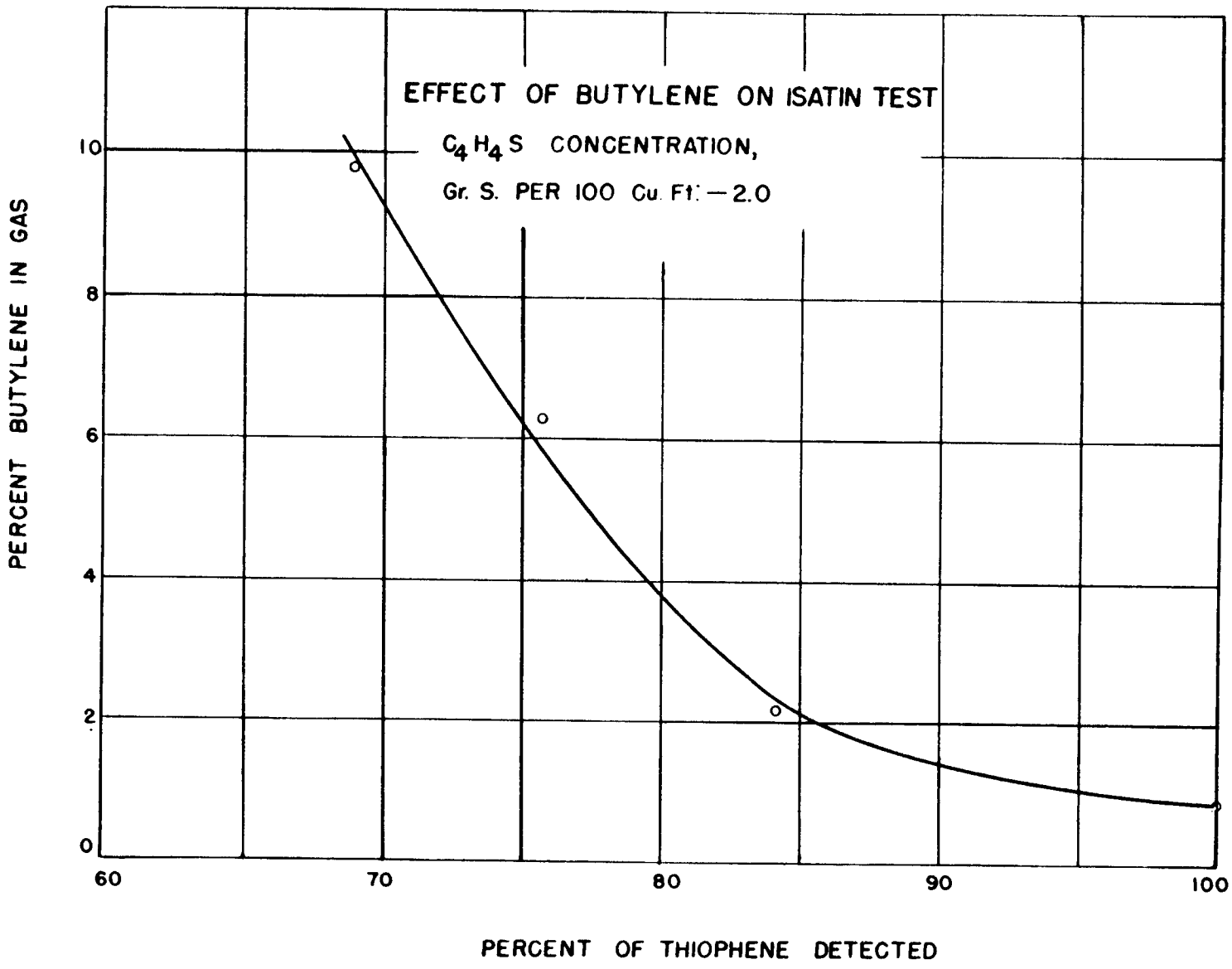

Figure 5. - Effect of butylene on isatin test.

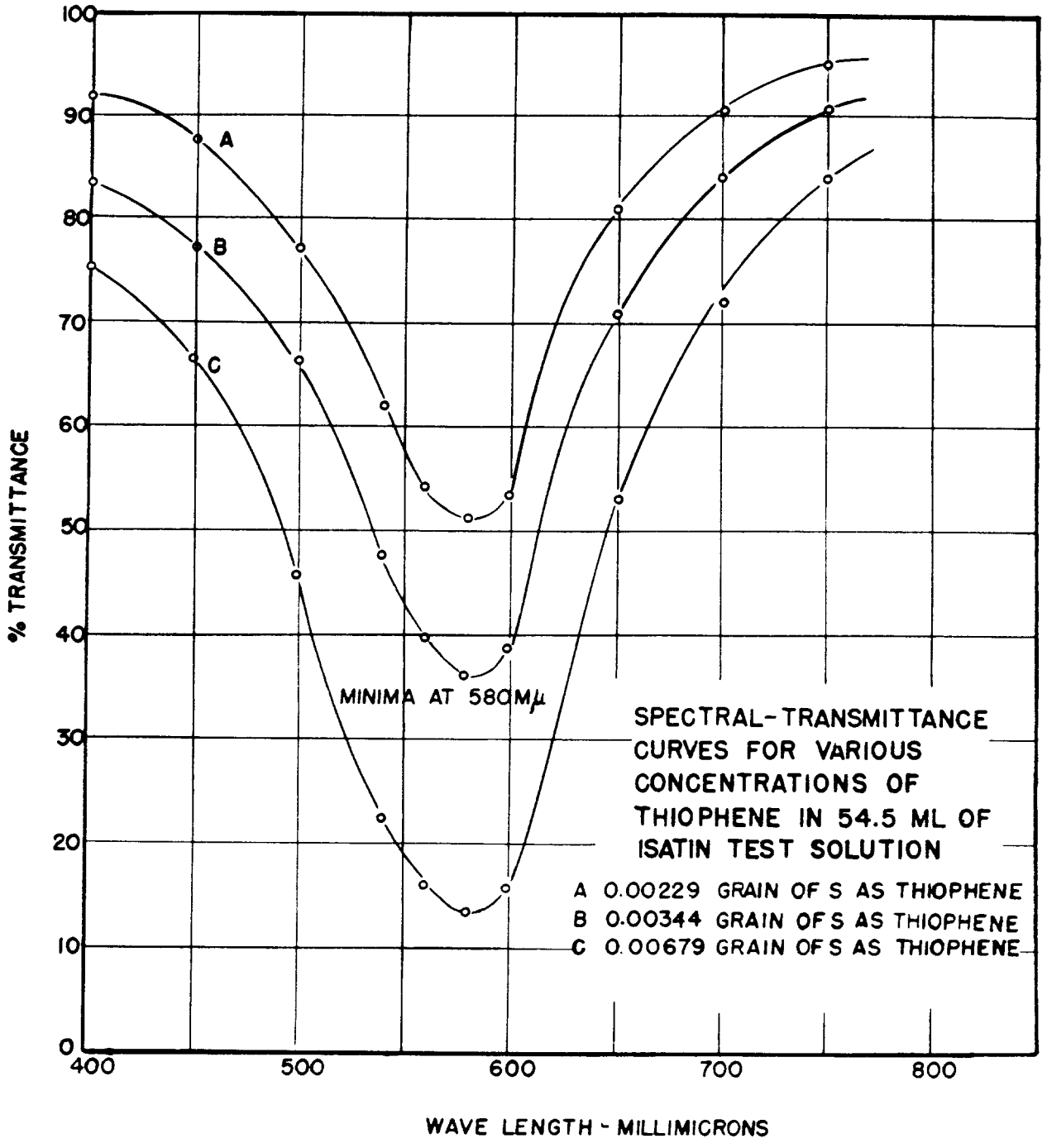

Figure 6. - Spectral transmittance curves.

Ethylene in gas, percent	Gr. S as C_4H_4S/100 cu. ft.	
	Actual	Isatin determination
1.9	0.24	0.21
1.0	.105	.085
3.1	.24	.14

Data from these runs as well as from those used in preparing the curve for ethylene (fig. 3) indicate that the ethylene content must not exceed 2 to 3 percent if worthwhile results are to be obtained.

Applicability to Synthesis Gas

The results from the original tests on the effect of unsaturated hydrocarbons, in which large quantities of the compounds were used, were a cause of concern, as gas produced from coal almost always contains unsaturated hydrocarbons. However, the result from the tests made to determine the tolerable amounts that could be present in gas and still render the test effective were quite encouraging, as the unsaturated hydrocarbons in the synthesis gas produced at this station are well within these limits. Data from 32 gasification runs show that the unsaturated hydrocarbon content of the synthesis gas ranges from 0 to 1.8 percent, the average being 0.7 percent.

Results from tests using the isatin method showed that there was no thiophene in the synthesis gas. It was thought that some constituent in the gas may be interfering with the method, but a test in which a known amount of thiophene was added to the gas stream proved the method valid, as the experimental value agreed with the actual sulfur value.

Procedure

Reagents

1. Isatin Reagent. Add 1.104 grams of isatin and 1.104 grams of ferric sulfate to a liter of distilled water. Heat to 85° C., cool to room temperature, and allow to stand for 24 hours before filtering off the excess isatin and ferric sulfate.

2. Sulfuric Acid. Concentrated, sp. gr. 1.84.

Color Measurement

Color intensity is measured spectrophotometrically with a Beckman spectrophotometer using a Beckman corex cell with a 10-mm. light path.

Figure 6 gives spectral-transmittance curves for test solutions containing various concentrations of thiophene. The optimum wave length is 580 millimicrons.

Calibration Curves

Standard samples were first prepared by adding known amounts of thiophene to a solvent and then adding a measured amount of these stock solutions to the isatin-acid solution. Solvents included benzene, ether, alcohol, acetone, and others. Results were so anomalous that this method of preparing standards was discontinued.

The method that was adopted and that gave excellent results was that in which thiophene was dissolved in dibutyl phthalate. The desired thiophene concentrations were obtained by bubbling measured quantities of gas through the solution. The dibutyl phthalate solution was maintained at a constant temperature.

The isatin-acid solution was prepared and allowed to age for 1 hour. The carrier gas was bubbled first through the thiophene fouling bottle, then through the isatin-acid solution, maintained at a predetermined temperature, and finally metered with a wet test meter. The concentration of thiophene in the carrier gas was determined by the platinum spiral method,23/ the resulting hydrogen sulfide being determined colorimetrically by using the methylene blue method.24/

When the desired concentration of thiophene had been absorbed by the test solution, the gas flow was discontinued. The transmittance of the solution was then measured with the spectrophotometer until the minimum transmittance (maximum color) had been reached.

Figure 7 gives calibration curves at various test-solution temperatures.

Determination of An Unknown Sample

4.5 ml. of the isatin-ferric sulfate solution is added to an 8- or 10-inch test tube. Fifty ml. of concentrated sulfuric acid is added slowly to the isatin-ferric sulfate solution. To prevent any charring, cold water is run over the test tube when the sulfuric acid is being added. After the acid is added, the isatin-acid solution is aged for 1 hour. While aging, the solution is brought to the temperature at which the determination is to be made.

The test tube is equipped with a gas inlet tube, which extends to the bottom of the test tube, and a gas outlet tube. The gas to be tested is first passed over iron oxide shavings to remove hydrogen sulfide, bubbled through alkaline $CdCl_2$ to remove mercaptans, bubbled through the isatin-acid solution, and then metered with a wet test meter. The gas flow is stopped whenever the test solution turns blue.

23/ See footnote 3.

24/ Sands, A. E., Grafius, M. A., Wainwright, H. W., and Wilson, M. W., The Determination of Low Concentrations of Hydrogen Sulfide in Gas by the Methylene Blue Method: Bureau of Mines Rept. of Investigations 4547, 1946.

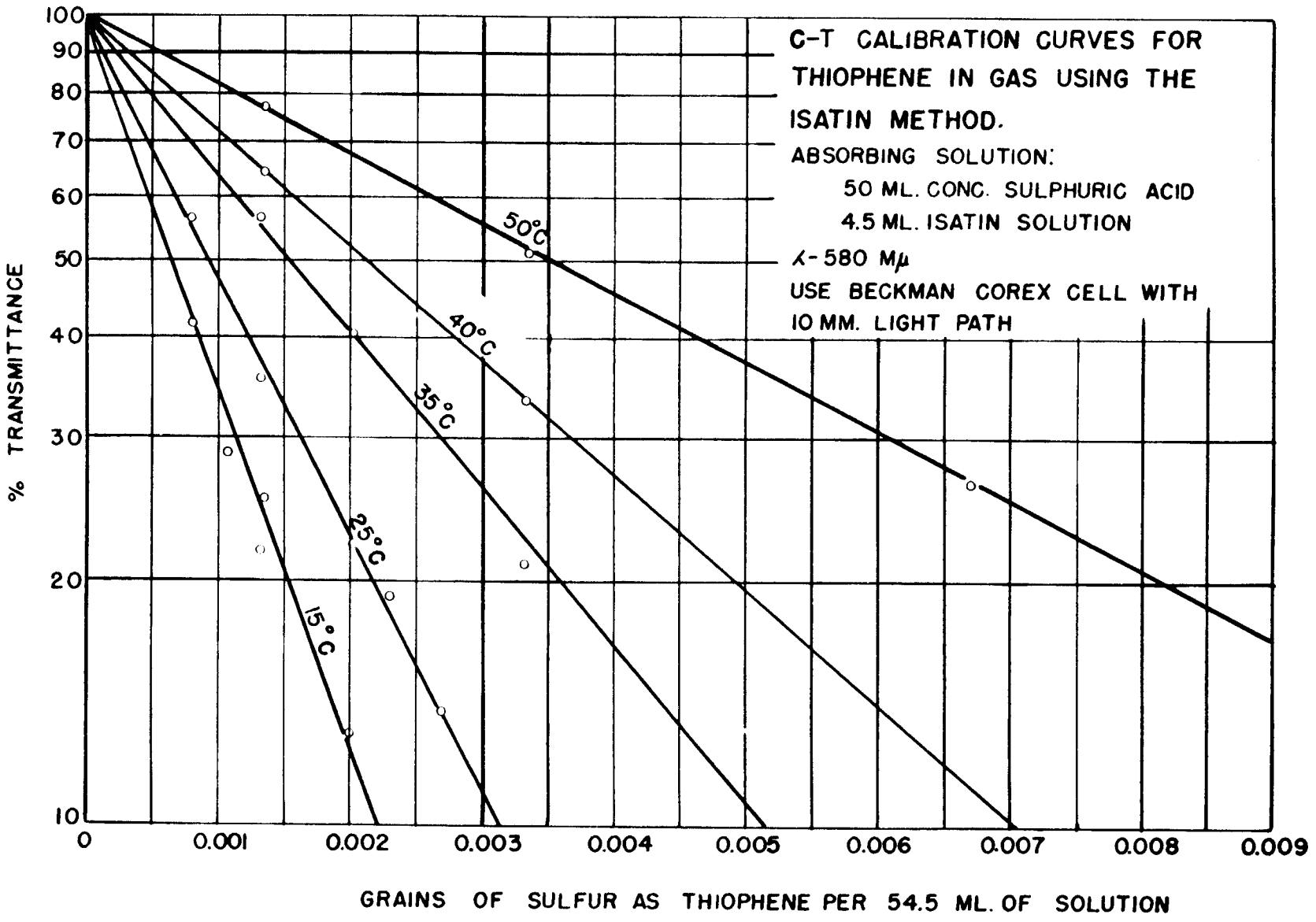

Figure 7. - C-T calibration curves.

A portion of the sample is then transferred to a Beckman corex cell, 10-mm. light path, and the minimum transmittance is read with a spectrophotometer by using a wave length of 580 millimicrons. The grains of sulfur per 54.5 ml. of test solution are read directly from the calibration curve. Knowing the quantity of gas tested, the concentration in grains per 100 cubic feet can be calculated.

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