INTRODUCTION

The Bureau of Mines, U. S. Department of the Interior, at its Morgantown, W. Va., station, operating under a cooperative agreement with West Virginia University, is conducting research and development work on the problem of producing synthesis gas from coal. An important part of this work is the study of the gas purification necessary to meet the rigorous standards required to render the gas suitable for use in the Fischer-Tropsch synthesis of liquid fuels.[4]

One of the most detrimental impurities is sulfur in all forms, the maximum amount that can be tolerated being one-tenth of a grain per hundred cubic feet. Concentrations as low as this require the use of precise analytical methods to evaluate the performance of processes used for removing sulfur. At the same time the analytical methods should be rapid in order to reveal the failure of purification before damage to the expensive synthesis catalyst results.

Although sulfur in unpurified gas is generally present as hydrogen sulfide and as organic sulfur compounds, the latter may be converted to hydrogen sulfide for analytical purposes. Thus, a suitable method for the determination of traces of hydrogen sulfide may also be used for the determination of organic sulfur.

After an extensive review of the literature, it was decided that the colorimetric methylene blue test appeared to be most promising, and laboratory investigations employing a photoelectric colorimeter and a spectrophotometer were made with a view toward applying this method to our work.

SUMMARY AND CONCLUSIONS

1. As little as 0.00001 grain of sulfide sulfur per 50 ml. of solution can be detected by the methylene blue test. This amount of sulfur is equivalent to 0.001 grain per hundred cubic feet when the gas sample is 1 cubic foot.

2. The reproducibility of this test applied to identical samples is ±0.000005 grain of sulfide sulfur per 50 ml. of solution.

3. This test has been applied to synthetic mixtures of carbon monoxide and hydrogen from cylinders. A limited number of tests on coke oven gas, carburetted water gas, and blue water gas indicates that the method is suitable for these gases also.

4. Mercaptans, carbon disulfide, and thiophene do not interfere. Mercaptans do give a pink color in this method, but this effect is eliminated by the use of a light source of the proper wave length.

5. The preferred absorbent for hydrogen sulfide in this method is 2 percent zinc acetate solution.

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[4] 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. 607-20.

6. Both the hydrochloride and the sulfate of p-amino-dimethylaniline, in varying concentrations, were studied, and different acid mixtures were used. Best results were obtained from the use of 0.15 gram of the sulfate dissolved in 150 ml. of 2:1 H_2SO_4. This reagent is stable for several days.

7. The proper wave length for use with the spectrophotometer is 745 millimicrons. Of the standard filters for use with the Klett-Summerson photoelectric colorimeter, the most suitable was found to be red filter No. 66.

8. A test procedure is presented, details of which must be followed scrupulously. Samples should be tested within 2 hours after termination of gas scrubbing. The sample should be cooled to 10°C. before adding the amine-acid reagent. At higher temperatures, lower values for sulfur are obtained, probably owing to springing of hydrogen sulfide before the reaction is completed.

9. Low concentrations of hydrogen sulfide in gas can be determined rapidly. When the gas contains 0.05 grain of sulfur as H_2S, only one-tenth of a cubic foot of gas need be passed, and the result is obtained in less than 30 minutes.

DISCUSSION

Many methods are available for determining hydrogen sulfide in gas; most of these are either not applicable to low concentrations or require the use of large samples of gas that require a long sampling period.

Lead acetate paper employing either neutral or basic lead acetate solution has long been used as a qualitative test. There is lack of agreement in the literature on the sensitivity of this test, probably owing to differences in experimental conditions and techniques employed by various investigators. The National Bureau of Standards[5] found that 0.2 grain per hundred cubic feet is the lowest concentration detectable after a 30-minute exposure. Leroux[6] found that the minimum concentration detectable varied according to the diluent gas, being 0.05 grain per hundred cubic feet in hydrogen, 0.13 grain in nitrogen, and 1.6 grains in carbon dioxide. Truesdale[7] found that the lowest hydrogen sulfide concentration giving a definite test was 0.012 grain per hundred cubic feet, whereas 0.002 grain gave no stain regardless of the amount of gas impinging on the paper.

Methods have been proposed by which the lead acetate paper test may be made quantitative, but in view of the foregoing data on variances in

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[5] McBride, R. S., and Edwards, J. D., National Bureau of Standards, Tech. Paper 41, 1914, 46 pp.

[6] Leroux, H. J., (Sensitivity of Lead Acetate Paper for Hydrogen Sulfide): Jour. Usines Gaz., vol. 55, 1931, pp. 117-22.

[7] Truesdale, E. C., Sensitivity of Various Tests for Traces of Hydrogen Sulfide: Ind. Eng. Chem., anal. ed., vol. 2, 1930, pp. 299-302.

sensitivity, these may be questionable under certain conditions. The hydrogen sulfide recorder invented by Moses and Jilk[8], on the other hand, is reported to give excellent results - determining as low as 0.005 grain per hundred cubic feet - and this instrument employed a lead acetate-impregnated tape, with the stain measured photoelectrically. This instrument[9] is probably too expensive for many laboratories ($4,000) and in any event does not lend itself to tests in several locations owing to lack of portability.

Other colorimetric tests include the nitroprusside[10] test and two methods of Field and Oldach[11]. These methods give good results but are open to the objection that sodium hydroxide is used as an absorbent. Our laboratory as well as previous investigators have found that such solutions are quickly oxidized by the air, and accurate results require rapid and careful technique. The vapor pressure of hydrogen sulfide from alkaline absorbents, although very low when the sulfide concentration is low, is still probably a source of error. Absorbents yielding an insoluble precipitate probably are preferable.

The more sensitive of the two methods of Field and Oldach determines the sulfide by means of a spectrophotometer after conversion of the sulfide to bismuth sulfide. By this method as little as 0.7 p.p.m. of sulfide sulfur can be determined with a precision of ±10 percent. Our laboratory confirmed the results obtained by the originators of the method.

References in the literature have claimed that the methylene blue test is the most sensitive test for hydrogen sulfide in solution. This test was first proposed by Emil Fischer[12] in 1883. Various investigators since that time have studied this method, generally applying it to water analysis, as, for example, sewage and sulfur spring water and in some cases to biological materials.

In the work of Fischer, 1 liter of water containing as little as 0.000018 gram of H_2S was treated with 20 ml. of concentrated HCl, 0.005 gram of p-aminodimethylaniline sulfate, and two drops of a dilute ferric chloride solution. A blue color developed after 30 minutes and was permanent for days. Fischer apparently proposed this method as a qualitative test only.

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[8] Moses, D. V., and Jilk, L. T., U. S. Patent 2,232,622.

[9] Communication from the Rubicon Co., Philadelphia, Pa.

[10] Currie, W. A., Jr., Some New Methods for the Control of Dry Purification: Gas World, vol. 99, 1933, pp. 553-7.

[11] Field, E., and Oldach, C. S., Determination of Hydrogen Sulfide in Gases: Ind. Eng. Chem., anal. ed., vol. 18, 1946, p. 665.

[12] Fischer, E., (Formation of Methylene Blue as a Reaction to Hydrogen Sulfide): Ber., vol. 16, 1883, pp. 2234-2236.

Lindsay[13], in 1901, applied the methylene blue test to the determination of sulfur in pig iron, whereby the sulfur was evolved from the iron as hydrogen sulfide and absorbed in sodium hydroxide solution. Lindsay used the p-aminodimethylaniline hydrochloride instead of the sulfate, as in Fischer's work, and made color comparisons with standards in Nessler tubes. Instead of hydrochloric acid, dilute sulfuric acid was used. As little as 0.00003 gram of sulfide-sulfur in 50 ml. of solution was reported to give excellent reproducibility.

The most thorough study of the method found in the literature was that of Mecklenburg and Rosenkranzer[14] in 1914. Their procedure employed varying sizes of samples diluted to 490 ml. This dilution was treated with 10 ml. of concentrated HCl, 0.05 gram of p-aminodimethylaniline sulfate, and 2.0 ml. of tenth molar ferric chloride solution. A visual colorimeter was used for comparing colors. A careful study was made of variables affecting the test. It was found that decreasing the amount of diamine decreased the color intensity produced. Temperature fluctuations of more than 2°C. were avoided, as lower temperatures gave greater color intensity. The presence of other electrolytes was found to have no effect on color intensity. As little as 0.01 p.p.m. of H_2S in solution could be detected. Three hours were required to develop the color when the concentration was 0.2 p.p.m.

Almy[15], in 1925, applied the test to hydrogen sulfide evolved from biological samples. The hydrogen sulfide was absorbed in 0.6 percent zinc acetate solution. The reagent used was 0.04 gram of p-aminodimethylaniline hydrochloride in 100 ml. of 1:1 HCl. The ferric chloride used was 0.02 molal. Color comparisons were made in Nessler tubes.

Sheppard and Hudson[16], in 1930, applied the test to biological materials, using the diamine sulfate dissolved in 1:1 HCl. No innovations were made in the method for developing the methylene blue; the work dealt principally with the procedure for evolving hydrogen sulfide from the gelatin or protein sample. The evolved H_2S was absorbed in alkaline zinc acetate solution.

Pomeroy[17], in 1936, applied the methylene blue method to sulfides in sewage. The reagent was prepared by dissolving 20 grams of freshly purified

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[13] Lindsay, W. G., On a Colorimetric Method for the Estimation of Sulfur in Pig Iron: Columbia School of Mines Quarterly, vol. 23, 1902, pp. 24-27.

[14] Mecklenburg, W., and Rosenkranzer, F., (Concerning a Method for the Colorimetric Determination of Small Amounts of Hydrogen Sulfide): Zeit. anorg. Chem., vol. 86, 1914, pp. 143-153.

[15] Almy, L. H., A method for the Estimation of Hydrogen Sulfide in Proteinaceous Food Products: Jour. Am. Chem. Soc., vol. 47, 1925, pp. 1381-90.

[16] Sheppard, S. E., and Hudson, J. H., Determination of Labile Sulfur in Gelatin and Proteins: Ind. Eng. Chem., Anal. ed., vol. 2, 1930, p. 73.

[17] Pomeroy, R., An Improved Method for the Determination of Sulfides: Water Works and Sewerage, vol. 83, 1936, pp. 279-81.

p-aminodimethylaniline in 100 ml. of concentrated HCl. Two ml. of this solution were added to 50 ml. of concentrated H_2SO_4 and 48 ml. of H_2O.

Burton[18], in 1936, was the first investigator to report the application of the methylene blue test to the determination of hydrogen sulfide in gas. The procedure of Sheppard and Hudson was used in developing the methylene blue color and for absorbing H_2S from gas. Burton made the innovation of using a photoelectric colorimeter for determining the color intensity. The colorimeter was fabricated in the laboratory. Sensitivity as low as 0.005 grain of sulfide sulfur in 250 ml. of sample can be detected.

Snell[19], in his book on colorimetry, recommends Almy's procedure.

INVESTIGATIONS AT MORGANTOWN

The need for an ultra-sensitive method for determining hydrogen sulfide - particularly in connection with analyses for organic sulfur by methods in which the organic sulfur was converted to hydrogen sulfide - first suggested the use of the methylene blue test. The method of Oldach and Field[20] was tried and found satisfactory, except that some trouble was experienced with the alkaline solution of the sulfide becoming oxidized by the air. Snell's[21] methylene blue procedure (after Almy) used zinc acetate as an abosrbent, and as this solution has a slightly acid reaction, it was decided to investigate the method. Instead of using visual color standards in Nessler tubes, it was decided to make use of the Klett-Summerson photoelectric colorimeter. A calibration curve was prepared, and results at first appeared to be satisfactory. After some months, gross discrepancies appeared, and the need for further investigation became obvious. The work of previous investigators was reviewed, and laboratory tests were made of their various procedures.

Study of Variables Affecting Method

Effect of Amount of Amine Used

The necessity for further work was indicated by the fact that known sulfide concentrations failed to give as great color intensities as had been obtained some time previously. This was found to be caused by a limited deterioration of the solid p-aminodimethylaniline hydrochloride used in preparing the reagent. It was found that by doubling the concentration of the p-aminodimethylaniline hydrochloride solution, the color intensities were increased to the values that had been obtained previously. This means that the loss in strength of the solid amine was compensated for by using twice as much in preparing the acid solutions of the amine. Further increases in concentration of the amine solution had no effect. Results of these tests on a sulfide solution follow:

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[18] Burton, M. T., Photocolorimeter for Determination of Hydrogen Sulfide in Natural Gas: Gas, vol. 12, 1936, pp. 41, 60, 62.

[19] Snell, F. D., and C. T., Colorimetric Methods of Analysis: D. Van Nostrand Co. Inc., New York, vol. I, 1936, pp. 593-6.

[20] See footnote 11.

[21] See footnote 19.

Gm. diamine-HCl per 150 ml. solution	Klett reading
0.03	222
0.05	286
0.10	340
0.15	340

It was decided to use diamine solutions containing 0.15 gm. per 150 ml. of acid, as, even if some further deterioration of the solid diamine were to occur, it would be compensated for by the 50 percent excess in quantity over the amount required to give a maximum reading.

Comparison of the Hydrochloride and Sulfate of the Diamine

As some previous workers had used the hydrochloride salt and some had used the sulfate, comparisons were made of colors obtained from using these salts to determine whether one or the other was preferable. With a given sample, identical color values were obtained with the two salts. With the hydrochloride, however, the color development was more rapid than with the sulfate, maximum values being obtained within 5 minutes, even for the high sulfide concentrations. After reaching a maximum color intensity, the samples containing the hydrochloride salt faded in color almost immediately. In low concentrations, this fading was more pronounced. The samples containing the sulfate salt do not fade appreciably, even overnight.

Blank Values

In conducting tests, the photoelectric colorimeter is set at zero, with a blank in the cell compartment. Ordinarily, color present in this blank should make no difference, as the instrument is adjusted to compensate for this. Using the hydrochloride salt in making the test results in colors that fade, as has been explained. With samples of low sulfide concentration (when the hydrochloride indicator is used) the maximum color is reached and begins to fade in less time than that required for the blank value to become constant. Thus, a given low-sulfide sample may begin to fade within 5 minutes, whereas the blank used for setting zero on the instrument would require a much longer time to become constant.

It is obviously desirable to use a constant-value blank for setting zero on the instrument, and yet it is equally obvious that a sample reading cannot be taken after 4 or 5 minutes (in order to read maximum value) if the blank used for comparison had required 15 minutes or more to become constant.

The following data show changes in colorimeter scale readings for a blank in which the hydrochloride salt was used, the instrument having been set at zero with distilled water in the cell compartment:

25°C.		10°C.	
Time, min.	Klett reading	Time, min.	Klett reading
1.5	16.5	1.5	25.3
2.0	14.3	2.0	24.0
2.5	12.5	2.5	22.0
3.0	11.3	3.0	20.5
3.5	10.0	3.5	19.8
4.0	9.0	4.0	18.5
4.5	8.5	4.5	17.8
5.5	7.3	5.5	15.5
6.5	6.5	6.5	14.0
7.5	5.5	7.5	13.0
9.5	4.3	9.5	12.8
10.5	4.0	10.5	10.5
13.5	3.5	13.5	9.0
15.0	3.5	15.0	6.5
		25.0	5.5
		36.0	4.0
		57.0	4.0

The tests at the two temperatures show that the same blank value is ultimately reached, whether the color is developed at room temperature or at 10°C., so that for preparing a blank no particular attention need be paid to temperature. Later it will be shown that samples should be cooled to 10°C. or below.

A similar test with the sulfate salt of the diamine gave constant blank values after about 3 minutes. Thus, especially for samples of extremely low sulfide content, the sulfate salt is to be preferred, as fading does not occur, and, also, blank effects become constant almost immediately. This results in greater sensitivity and reproducibility.

Temperature

Mecklenburg and Rosenkranzer[22] stated that temperature should not vary more than 2°C. in carrying out the test, and that lower temperature gave greater color intensities.

The present authors noted that on adding the acid solution of the diamine salt, the solution warmed up, owing to the heat of dilution of the acid. The effect of temperature upon color intensity, cited above, was confirmed in the present work.

The following data, all for aliquots of a single sample, illustrate this effect:

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[22] See footnote 14.

Temperature °C. before reagent addition	Temperature °C. after reagent addition	Klett reading
30	40	450
25	33	470
20	30	485
15	25	495
10	19	500
6	15	500

The foregoing data show that if the sample is cooled to 10°C. before adding the acid amine reagent, a maximum color effect is obtained. Presumably, the higher temperatures result in a loss of H_2S owing to the higher vapor pressure of the H_2S from the solution of those temperatures.

Changes in temperature after the color is developed have no effect upon color intensity, so that no precautions need be taken with respect to temperature after the reagent is added to the sample.

Interfering Substances

Snell,[23] in his book, repeated the statement of Almy[24] that mercaptans do not interfere because they are not absorbed in zinc acetate. The present authors found, however, that ethyl mercaptan is absorbed by either 0.6 or 2.0 percent zinc acetate solution, a white precipitate of zinc mercaptide being formed.

With ethyl mercaptan present, a pink color is formed on adding the diamine reagent. This pink color is different from the transitory pink color experienced during methylene blue formations from sulfides. Interference due to this pink color is minimized by proper filter selection (or proper wave length with the spectrophotometer), so that no significant change in colorimeter reading results.

The pink color due to mercaptans can be measured by use of a green (Klett No. 50) filter. A sample containing 0.0008 grain of sulfur as ethyl mercaptan in 50 ml. gave a Klett reading (using the green filter) of 199. This same amount of mercaptan added to a sulfide sample gave no change in colorimetor reading when the red (Klett No. 66) filter was used. The data follow for 50-ml. samples and Klett No. 66 filter:

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[23] See footnote 19.
[24] See footnote 15.

Gr. S as H_2S	Gr. S as C_2H_5SH	Klett reading
0.000281	-	252
0.000281	0.00033	258
0.000265	-	195
0.000265	0.00134	193
0.000057	-	64
0.000057	0.0008	64
0.000561	-	465
0.000561	0.00066	455

Similar tests were made to determine whether carbon disulfide or thiophene affected the methylene blue test. Data follow:

Gr. S as H_2S	Gr. S as CS_2	Klett reading, #66
0.000057	-	54
0.000057	0.0016	52
0.00015	-	166
0.00015	0.0016	168

Gr. S as H_2S	Gr. S as C_4H_4S	Klett reading
0.000127	-	136
0.000127	0.0012	132
0.000127	0.0024	125
0.000127	0.0048	116

The foregoing data show that no appreciable effect upon the test results from the presence of ethyl mercaptan or carbon disulfide. Thiophene has no appreciable effect except when present in a concentration about 40 times that of the sulfide; then the effect is to give somewhat lower results.

Applicability to Various Commercial Gases

It has been shown that the common types of organic sulfur compounds found in coke-oven gas, carburetted water gas, and natural gas do not seriously affect the test.

It has been found possible to develop the blue color from traces of hydrogen sulfide naturally occurring in coke-oven gas and carburetted water gas. Tests in which hydrogen sulfide was added to natural gas also gave the characteristic reaction. Tests with these gases also showed that no blue color was developed when the gas was absolutely free of hydrogen sulfide.

No comparative tests were made with these commercial gases to determine the precision of the methylene blue method when used on these gases. Such comparative tests could be made by using large samples of gas containing a trace of hydrogen sulfide and one of the better methods, such as the iodimetric method of Shaw,[25] and small samples of the same gas with the methylene blue method.

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

Range of Test

The Klett-Summerson colorimeter, owing to its logarithmic scale, gives better results for scale readings not exceeding 400. Actually, the authors prefer to work with samples of such dilutions that scale readings of 100 to 200 result. However, closely reproducible results may be obtained at as low as 15 scale units or as high as 450 scale units.

Color intensities that do not exceed 500 scale units on the Klett instrument can be diluted with resulting proportional changes in instrument reading. It is not possible, however, if the color intensity is greatly in excess of 500 - for example off-scale - to bring the color intensity within range by diluting, as results that are too low will result. This is probably explained by the fact that an insufficient excess of reagent is present in such cases, and also by a possible loss of H_2S from more concentrated solutions due to the H_2S vapor pressure from the solution.

Age of Reagent

Some previous investigators have prescribed the use of freshly prepared diamine reagent. The present authors have found this to be true in some cases when working with the more dilute reagent (0.05 gm. of diamine hydrochloride in 150 ml. of solution). However, when the solution containing 0.15 gm. in 150 ml. is used, age has little effect on the reagent, as shown in the following data. These data show Klett readings for identical samples made with freshly prepared reagent and reagents of various ages that had been stored at room temperature:

Klett reading, fresh reagent	Klett reading, old reagent	Age of old reagent, days
560	560	1
174	172	3
340	335	14
480	460	24

The foregoing data show that reagent may be kept for at least 1 week and perhaps longer. As a further precaution, it might be advisable to keep the reagent in a refrigerator.

Age of Sample

Samples used in this investigation were prepared by adding aqueous H_2S solutions to various absorbents for H_2S, as described elsewhere in this paper. The resulting mixtures were permitted to age over several hours or days, and tests were run at intervals to determine the effect of age upon the samples.

Samples that had aged not over 2 hours invariably showed no appreciable change. Those aged longer behaved erratically, generally showing appreciable decrease in sulfide. Storing samples in a refrigerator sometimes seemed to preserve them, and sometimes losses on aging were not proportional to concentration. No particular absorbent for H_2S seemed to be better than another with respect to stability on aging. Samples that had been treated by bubbling hydrogen or nitrogen through them and that had been sealed under slight pressure of the gas used showed similar effects on aging. Some of the very considerable data taken on aging of samples follow:

Absorbent	Fresh sample, Klett reading	Aged samples, Klett reading	Age of sample	
2% $ZnAc_2$	480	480	2 hr.	
Do.	480	480	4 hr.	
Do.	480	475	6 hr.	
Do.	139	109	8 hr.	
Do.	300	288	1 day	
Do.	350	350	2 hr.	
Do.	310	252	1 day	
Do.	214	166	2 days	
0.6% $ZnAc_2$	370	350	1 day	
Do.	174	148	1 day	
Do.	370	300	10 days	
Do.	510	445	5 days	
0.3% alk. $CdCl_2$	325	250	2 days	
Do.	325	136	5 days	
Do.	325	310	1 day	
Do.	475	390	1 day	
10% alk. $CdAc_2$	194	184	16 hr.	
Do.	330	270	14 hr.	
Do.	350	325	18 hr.	
10% alk. $CdCl_2$	115	102	16 hr.	Stored under H_2
10% alk. $CdAc_2$	176	150	12 hr.	
10% alk. $CdAc_2$	288	264	18 hr.	Stored under N_2
10% neut. $CdAc_2$	131	108	14 hr.	

The foregoing data point to the necessity of working with fresh samples for precise work. Although on a percentage basis the overnight losses are serious, these actually represent small losses in actual quantities of sulfur; e.g., a loss of even 50 Klett-scale units represents a loss of only 0.00003 grain of sulfur per 50 ml. of solution.

The explanation of this aging effect upon solutions is not clear. Among the theories considered have been air oxidation of the sulfide, transition to sulfides insoluble in acid, adhesion of some of the sulfide to the storage flask, H_2S vapor-pressure losses due to partial hydrolysis of the metal sulfides, and impurities in the distilled water or absorbent slowly reacting with the sulfide to yield a different form of sulfur compound or elementary sulfur. Laboratory investigations were made of these theories, without confirmation.

Regardless of the cause of this effect upon aging, the conclusion is that samples must be analyzed within 2 hours for highest precision. Also, it should be noted that regardless of the method used for determining sulfide sulfur in low concentrations, this same effect upon aging would prevail if the same absorbents were used. It is only because of the extreme sensitivity of the methylene blue test that those changes upon aging are detectable. It would obviously be impossible to detect an overnight change equivalent to 25 Klett-scale units (0.000015 grain sulfur) for a 50 ml. sample iodimetrically.

Absorbents for Hydrogen Sulfide

The present authors, as well as previous investigators, had found that alkaline solutions of H_2S were not stable, being rather rapidly oxidized by the air. It was desired, therefore, to avoid the use of sodium hydroxide as an absorbent, if possible, although Altieri[26] suggests that reagent as an absorbent for H_2S in the methylene blue test, as set forth in his book on gas analysis.

Almy[27] used 0.6 percent zinc acetate as an absorbent for H_2S in his methylene blue procedure for H_2S evolved from biological material, so it was decided to try the same absorbent for H_2S in synthesis gas. Almy had stated that the solution gave complete absorption of H_2S and that continued passage of carbon dioxide (used as sweep gas in his procedure) did not result in a loss of H_2S.

In the present work, it was decided to increase the strength of the zinc acetate to 2 percent to give increased assurance of complete absorption.

A series of experiments was run with 2 percent zinc acetate, varying gas rates, and varying H_2S concentrations. As a result, it was concluded that in an ordinary gas washing bottle a rate of as much as 1.8 cubic feet per hour could be used when the H_2S concentration did not exceed 13.5 grains per hundred cubic feet with complete absorption being obtained. Higher sulfide concentrations in gas were not investigated, because for such concentrations the ordinary iodimetric methods are satisfactory. Moreover, for high H_2S concentrations, if the methylene blue method were to be used, the amount of gas sample would be so small that an extremely slow rate of gas could be tolerated without unduly prolonging the test.

Tests were run with cadmium chloride and cadmium acetate - both neutral and alkaline - which were found to give complete absorption and to be amenable for subsequent use in the methylene blue test. However, the cadmium reagents give a heavier, more rapidly settling precipitate than does zinc acetate, and hence are not so satisfactory when it is desired to make dilutions. Zinc acetate yields a precipitate with H_2S that is almost colloidal when freshly formed. When the white precipitate of zinc sulfide first becomes apparent, more than enough sulfide is present for the methylene blue test. In fact, it is necessary, when a precipitate is perceptible, to dilute the sample in order to avoid exceeding the range of the photoelectric colorimeter.

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[26] Altieri, V. J., Gas Analysis and Testing of Gaseous Materials: Amer. Gas Assoc., Inc., New York, 1945, p. 353.

[27] See footnote 15.

One important observation not previously mentioned in the literature was the fact that zinc sulfide adheres to the sides of the gas-washing bottles even after rinsing with zinc acetate solution or distilled water. Such adhering sulfide is not usually perceptible to the eye, but if more zinc acetate is added and the diamine reagent is added with color development in the washing bottle, an appreciable amount of sulfide will be found. Following are test data illustrating this fact:

Klett reading, color developed in Klett cell	Klett reading, color developed in bottle
79	79
84	57
97	41

The above data are probably exceptional, as many tests were made in which no sticking to the flask occurred. In the above data, note that the color developed in the bottle results from the sulfide adhering to the bottle after rinsing. This sulfide was not visible.

In connection with the investigation of the sample-aging phenomenon already mentioned, experiments were made in which air and various inert gases were bubbled through zinc acetate and other absorbents having known sulfide contents. It was found that definite losses in sulfide content resulted and that these losses were as great when gas containing no oxygen (electrolytic hydrogen) was used as when air was used - proving that the loss was not due to oxidation from the gas stream.

One theory to explain this loss was that stripping was taking place - that the very small amount of sulfide soluble in the solution hydrolyzed and that H_2S was then carried out in the gas stream, with more sulfide then going into solution.

This theory is not confirmed by the data, as the losses were not greater at higher temperatures, and the losses were not proportional to the amount of stipping gas used, as might be expected with saturated solutions containing an excess of the solute.

The authors were concerned with this so-called "stripping" phenomenon, because this would seem to indicate that absorption could not be complete during actual tests on gas if an H_2S vapor-pressure equilibrium were permitting loss of H_2S in this manner. Attempts to recover such supposed losses in a second scrubbing bottle containing zinc acetate or cadmium chloride were unsuccessful, possibly confirming that true stripping was not occurring.

To insure that the electrolytic hydrogen did not contain traces of oxygen sufficient to oxidize the sulfide, the hydrogen in some tests was passed over hot metallic copper to remove any traces of oxygen that might be present.

A theory that arsenic might be present in the zinc and cadmium salts used for preparing the absorbents and that such arsenic might slowly convert the sulfide to acid-insoluble arsenic sulfide, thus giving lower values by the methylene blue test, was proved to be incorrect when a Gutzeit test was run on the zinc acetate and no arsenic was found.

Although these losses, shown in the following data, appear to be serious and perhaps are a cause of concern from a percentage-wise interpretation, the actual losses, in terms of grains per hundred cubic feet, are generally negligible, even for the rather exacting requirements for tests on purified synthesis gas. Thus, if the loss after passage of 1 cubic foot amounts to 25 Klett units (generally the loss does not exceed this figure), this loss is equivalent to 0.000015 grain of sulfur. In terms of grains per hundred cubic feet, this amounts to only 0.0015 grain. For the tests in which more than 1 cubic foot of gas was passed, the loss is even less. Thus, in one test the loss when 10 cubic feet of nitrogen were passed was 62 Klett units, equivalent to 0.00004 grain. For 100 cubic feet, this would equal 0.0004 grain of sulfur. Some of the data follow:

Absorbent	Gas used	Original Klett reading	Klett reading after-	
			1 cu.ft.	10 cu.ft.
1% Alk. $CdCl_2$	Air	345	320	-
10% Alk. $CdCl_2$	H_2	29	-	17
10% Alk. $CdAc_2$	Air	194	-	174
10% Alk. $CdAc_2$	H_2	194	-	176
10% Alk. $CdAc_2$	N_2	350	-	288
0.6% $ZnAc_2$	H_2	202	-	155
2.0% $ZnAc_2$	Air	100	-	92
2.0% $ZnAc_2$	H_2*	260	225	-
2.0% $ZnAc_2$	Nat. gas	240	-	224
2.0% $ZnAc_2$	Nat. gas	133	130	-
2.0% $ZnAc_2$	Nat. gas	141	121	-
2.0% $ZnAc_2$	Air	224	-	209
2.0% $ZnAc_2$	Air	83	47	
2.0% $ZnAc_2$	Nat. gas	286	260(10°C.)	
2.0% $ZnAc_2$	Nat. gas	286	260(35°C.)	

* In this test, electrolytic hydrogen was passed over hot copper to remove traces of oxygen.

Minimum H_2S Concentrations in Gas Determined by this Method

There are two limitations on the minimum concentration of H_2S in gas that this method can determine. One of these is the sensitivity of the test; the other is the fact that if the H_2S concentration is extremely low, more gas sample is required, and this will result in further loss of sulfide from the determination by the so-called "stripping" phenomenon. On the other hand, it is probably true that with the extremely low H_2S concentrations, less "stripping" loss will occur.

Assume that it is desired to obtain a Klett reading of 100. This is equivalent to 0.00006 grain of sulfur per 50 ml. of solution. If 10 cubic feet of gas were passed in order to collect this much sulfur, then the sulfur in the gas must have been 0.0006 grain per hundred cubic feet. If the "stripping" loss was 0.004 grain per hundred cubic feet, then the true value would have been 0.001 grain per hundred cubic feet and the error 40 percent - a serious error when considered from a standpoint of percentage, but not in terms of actual quantity of sulfur (0.0004 grain per hundred cubic feet).

If the error is to be reduced to 10 percent, then when a 10-cubic-foot sample is used the true sulfur content would have to be 0.004. Of course, such a sample would have to be diluted tenfold to reduce to the suitable range for the Klett instrument. Note that in the previous reasoning, the "stripping" loss was assumed to be 0.0004 grain per hundred cubic feet. Actually, this probably represents a maximum loss and usually will be much less. If this "stripping" loss were constant, suitable correction could be applied. However, the data show that the loss is erratic, so that only a maximum value for loss can be assumed.

If higher accuracy is required, for example, 1 percent, the minimum sulfur concentration that could be determined with this precision would be 0.04 grain per hundred cubic feet. The precision of the method, so far as reproducibility of color for identical sulfide concentrations is concerned, is high, as evidenced by close proximity of points to the calibration curve. It should be noted that deviations from the curve, to the extent that they occur, are due to discrepancies in the calibration technique, such as losses of H_2S from the aqueous solutions, errors in the iodimetric titration, etc. On identical samples, when the procedure is followed carefully, virtually identical readings are obtained.

Wave Length and Filter Selection

This work was begun before a spectrophotometer was available in the laboratory, and work was done with the Klett-Summerson photoelectric colorimeter. Hence, filter selection was made empirically, and the filter that gave best results was selected from those on hand. Klett filter No. 62 was found to be the best of those available, and much work was done with it. Later, when the Beckman spectrophotometer became available, a spectral-transmittance determination of the solution was made, and the optimum wave length was found to be 745 millimicrons (fig. 1). Using this wave length, a calibration curve giving percent transmittance for various concentrations was prepared (fig. 2). Actually, with a spectrophotometer, only one point other than 100 percent transmission is required to prepare a curve; additional points were plotted, however, to prove that the Lambert-Beer law applied. The deviations from the curve for individual points, although apparent, are really of a small order of magnitude. These deviations are noticeable, because the sensitivity of the instrument is much greater than the accuracy possible in the preparation of standards.

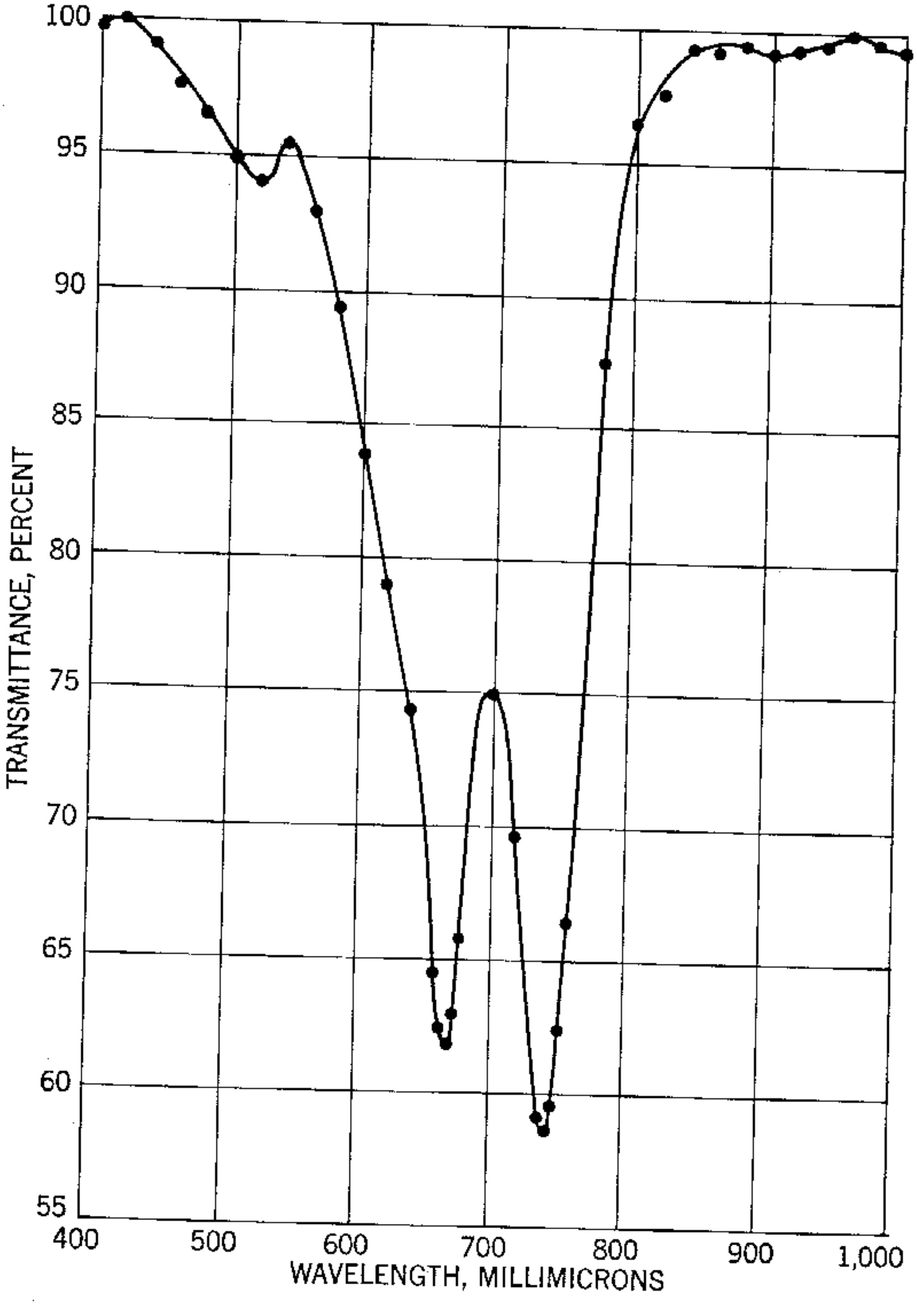

Figure I. - S-T curve of methylene blue.

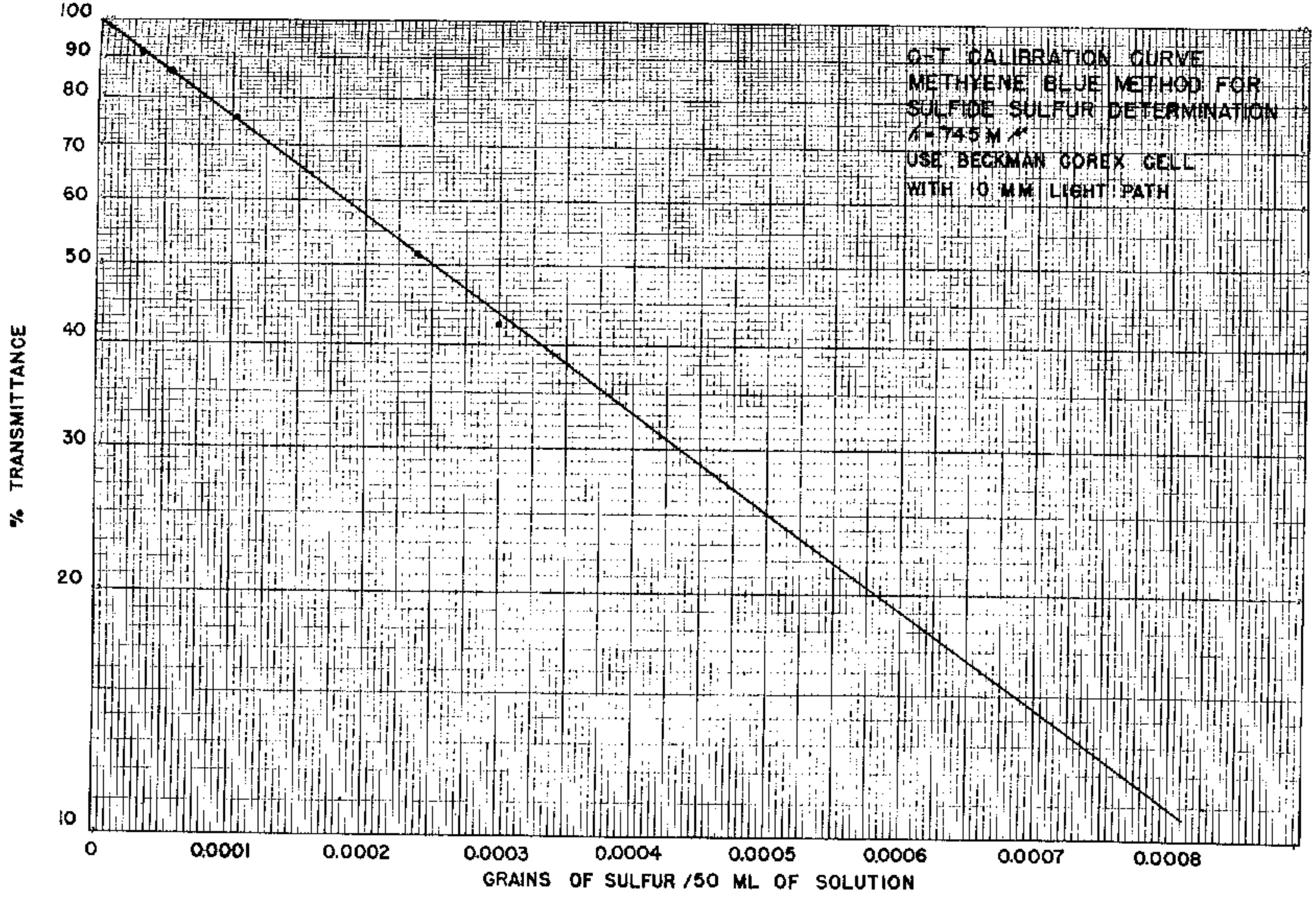
Q-T CALIBRATION CURVE
METHYENE BLUE METHOD FOR
SULFIDE SULFUR DETERMINATION
λ=745 Mμ
USE BECKMAN COREX CELL
WITH 10 MM LIGHT PATH
% TRANSMITTANCE
100
90
80
70
60
50
40
30
20
10
0
0.0001
0.0002
0.0003
0.0004
0.0005
0.0006
0.0007
0.0008
GRAINS OF SULFUR /50 ML OF SOLUTION

Figure 2.

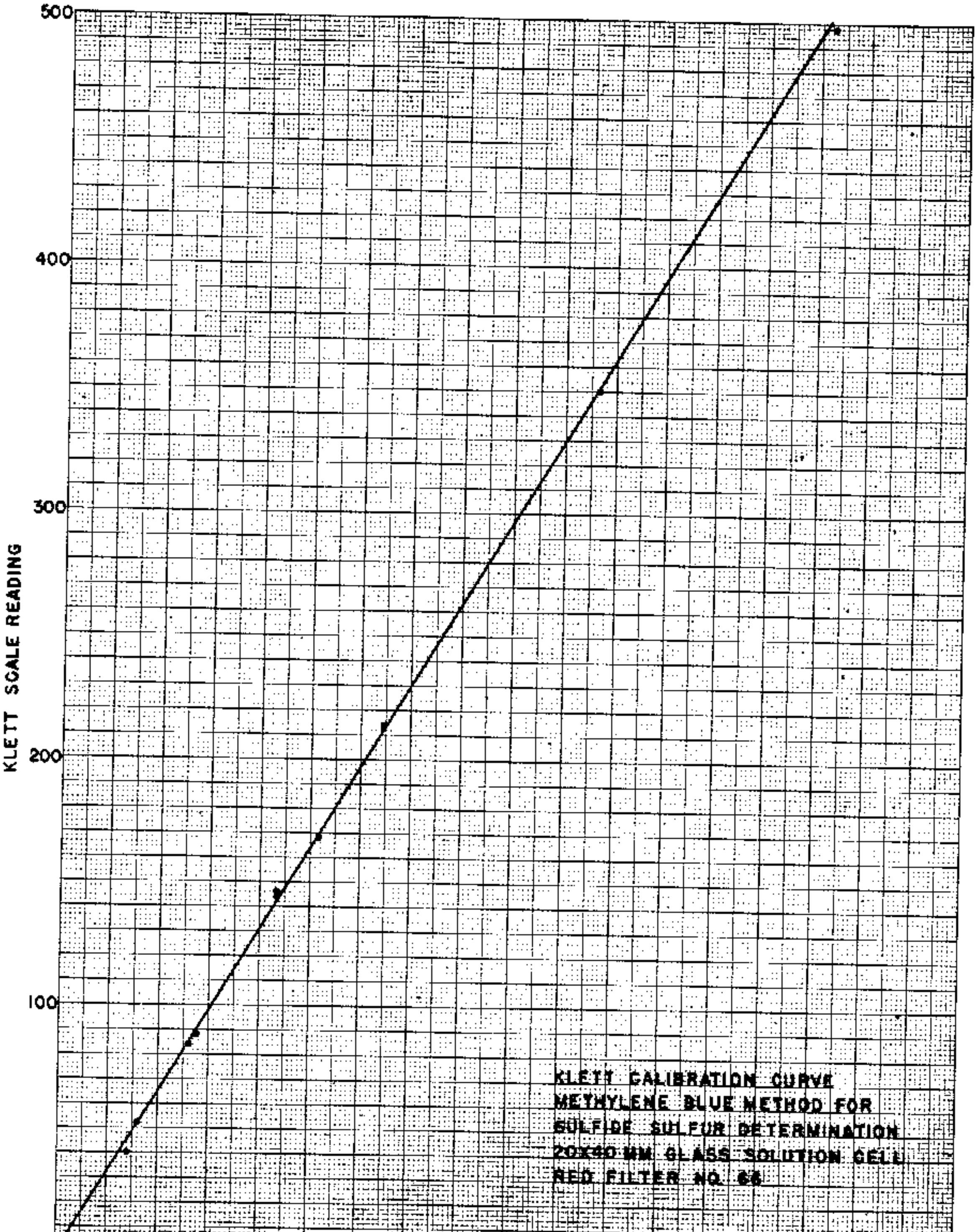
500
400
300
200
100
0
KLETT SCALE READING
0
0.0001
0.0002
0.0003
GRAINS OF SULFUR/50 ML OF SOLN.
KLETT CALIBRATION CURVE
METHYLENE BLUE METHOD FOR
SULFIDE SULFUR DETERMINATION
20X40 MM GLASS SOLUTION CELL
RED FILTER NO. 66

Figure 3.

With knowledge of the optimum wave length, it was decided to obtain additional filters for the Klett-Summerson colorimeter in order to use a more nearly correct wave length. When these were obtained, filters 66 (640-700 millimicrons) and 69 (660-740 millimicrons) were tested. Filter 69 should have approximated the optimum wave length as determined by the spectrophotometer, but Klett readings obtained with this filter were lower than those obtained from No. 66, which supposedly approximated the other minimum on the spectral transmission curve. Accordingly, filter 66 was used for the remaining work.

It should be noted that the calibration curve for the Klett-Summerson colorimeter (fig. 3) is included in this report for illustrative purposes only. Other laboratories having this instrument should prepare their own calibration curves, as there may be differences in the filters or instruments that would give different results. If a filter becomes broken and has to be replaced, the calibration should be repeated. Results approximating those in figure 3 should be expected, however.

The calibration curve given as figure 2 and the spectral transmittance curve given as figure 1 should be reproducible with any Beckman spectrophotomer.

Procedure

Reagents:

1. 20 percent zinc acetate aqueous solution.

2. 2 percent zinc acetate aqueous solution made from the 20 percent zinc acetate. Acidify each liter with approximately three drops of acetic acid.

3. Acid-diamine indicator - 0.15 gm. of p-aminodimethylaniline sulfate dissolved in a mixture of 100 ml. of concentrated sulfuric acid and 50 ml. of water which has been cooled previously to room temperature.

4. Ferric chloride solution - 2.7 gm. of ferric chloride hexahydrate dissolved in 50 ml. of concentrated hydrochloric acid and diluted to 100 ml. with water.

5. 0.1 N iodine.

6. 0.1 N sodium thiosulfate.

7. Starch indicator solution.

Curve Calibration:

Standard solutions containing a known amount of hydrogen sulfide are prepared in the following manner. Pipette 500 ml. of water into a 600 ml. beaker. Pass between 5 and 50 bubbles of hydrogen sulfide gas from a cylinder, depending on the concentration desired, into the water, with vigorous stirring. Pipette out 10 ml. of the hydrogen sulfide solution and place it in a 1-liter volumetric flask containing 100 ml. of 20-percent zinc acetate, about 800 ml. of water, and 3 drops of acetic acid. Make up the solution to volume with distilled water. Immediately upon withdrawal of the 10 ml. portion from the beaker, pipette 20 ml. of 0.1 N iodine into the remaining 490 ml. of hydrogen sulfide solution. Back-titrate the excess iodine with 0.1 N sodium thiosulfate, using starch indicator. Calculate the grains of sulfur present in 50 ml. of the zinc sulfide standard solution. All of this work should be done as quickly as possible.

The methylene blue color is developed in the following manner. Pipette 50 ml. of the standard zinc sulfide solution into a 20- by 40-mm. Klett cell and cool the solution to at least 10°C. in an ice-water bath; add 5 ml. of the acid-diamine indicator; stir gently; add 1 ml. of the ferric chloride solution; again stir gently and allow to stand between 15 and 30 minutes until maximum color development has taken place. Prepare a blank similarly. Use a No. 66 filter in the Klett-Summerson photoelectric colorimeter and zero the instrument with the prepared blank. Place the cell containing the color development in the instrument, balance the galvanometer, and read the scale, which is in Klett units. Frequent reblanking may be necessary.

Prepare a graph, plotting Klett units against grains of sulfur per 50 ml., from a collection of about 10 separate standard determinations. These points should result in a straight line.

Determination of Unknown Solution:

Use a wide-mouthed bottle, containing 50 ml. of 2 percent zinc acetate in which the hydrogen sulfide is to be absorbed, as a bubbling bottle. Pass the gas through the bubbling bottle until a faint turbidity forms in the zinc acetate solution. Then wash the contents of the bubbling bottle into a liter volumetric flask with 2 percent zinc acetate. Rinse out the bottle carefully several times. Develop the methylene blue color as described under curve calibration and observe the Klett reading. If the color developed produces a reading of more than 400 Klett units, make a suitable dilution and again develop the color. Apply the Klett reading to the graph to determine the amount of sulfur, incorporating the proper dilution factor. Add 50 ml. of 2 percent zinc acetate to the previously used bubbling bottle and develop the color in this bottle. In 15 minutes transfer the contents to a Klett cell, take a reading, and calculate the amount of sulfur in the same manner as before. Add the two determinations to obtain the total amount of sulfur in the sample. If it is inconvenient to obtain a sample containing this much sulfur, smaller dilutions may be made, or the color can be developed completely in the bubbling bottle.

The distilled water used throughout this method must be of good quality. The distilled water supplied to the laboratory in which this work was done was inferior, and it was necessary to use triple-distilled water.