TABLE 4. - Comparison of I.G.T.-Burner and modified Referees' Methods

Organic sulfur, S/100 cu. ft., gr.

I.G.T.	Modified referees'
0.012	0.016
1.03	.99
	1.03
	.97
	.99
2.46	2.39
2.56	2.61
2.46	2.33
2.63	2.33

I.G.T. Burner

The I.G.T. burner method developed by Hakewill and Rueck[8] represents a considerable improvement over earlier methods and has been adopted by the Morgantown Station of the Bureau of Mines for use whenever a burner method is indicated, but with some modifications.

These modifications consist of adding a third fritted-glass gas-washing bottle (even for low sulfur concentrations) and turbidimetric determination of barium sulfate. Addition of the third washing bottle permitted an increase in the gas rate from 0.5 to 1.8 cu. ft. per hour; this necessitated increasing the opening of the burner tip.

The following data are typical of the reproducibility of results obtained from the I.G.T. burner procedure as modified by the Bureau laboratory, figures representing grains of sulfur per 100 cu. ft. of gas for four different gas compositions:

0.015	0.31	2.46	11.70
.011	.37	2.56	11.90
.0097	.34	2.46	11.82
		2.63	

Gas used was a mixture of carbon monoxide and hydrogen from cylinders. Figure 1 shows the I.G.T. apparatus assembly in the Bureau's laboratory.

Rogers and Baldaste Method

The method of Rogers and Baldaste[9] was investigated because of the excellent results reported in the literature. This method included an

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

[9] Rogers, F. M., and Baldaste, R. F., Determination of Organic Sulfur in Combustible Gas: Ind. Eng. Chem., anal. ed., vol. 12, 1940, p. 724.

elaborate procedure for purifying the combustion air and for protecting the solutions from contamination during concentration. The procedure for purifying the air was found to be no better than that employed by the I.G.T. method, and the protection of the solutions by a curtain of purified air was found to be unnecessary, at least in the authors' laboratory.

The Rogers and Baldaste method does not provide for electrical ignition of the gas, a feature of the I.G.T. method. Moreover, only one gas-washing bottle is provided, which is clearly inadequate when working with gas containing a moderate concentration of sulfur.

One improvement incorporated in this method is the use of the Betz-Hellige turbidimeter for determining the small amounts of barium sulfate resulting. The procedure followed by Rogers and Baldaste in using the turbidimeter was that of Sheen, Kahler, and Ross.[10/] In applying the turbidimeter to other burner methods in the Morgantown laboratory, this procedure was found to require revision in order to obtain correct results.

Turbidimetric Determination of Sulfate

It was felt that substitution of the Betz-Hellige turbidimeter for the gravimetric determination of sulfate would contribute to the accuracy, and certainly to the convenience, of the Hakewill and Rueck method. Review of the literature revealed little of direct application to the Betz-Hellige turbidimeter for low sulfate concentrations except the work of Sheen, Kahler, and Ross in 1935.[11/] Use of sample cells in 50-mm. and 100-mm. sizes is not mentioned in their work, although these cells are now available. The filters supplied with the instrument have been changed since the time of their work.

In addition to investigating the use of the 50- and 100-mm. cells, which give more accurate results than those obtained from the 10- and 20-mm. sizes, this laboratory found it necessary to insure that enough sulfate (blank value) is present in the salt-acid solution used to provide for the barium sulfate saturation of the resulting mixture to be examined. With extremely pure reagents - most of the C.P. grades - barium sulfate resulting from the sulfur in the gas may partly escape detection owing to its solubility.

Laboratory experiments with standard solutions proved that as much as 0.000255 gram of sulfur, as sulfate, per liter may escape detection through the solubility of the resulting barium sulfate. This amount of sulfur is significant because it is equivalent to 0.05 grain of sulfur per 100 cu. ft. of gas when a sample amounting to 2 cu. ft. is burned and represents 50 percent of the total amount of sulfur permissible in purified synthesis gas.

Although, in the work of Sheen, Kahler, and Ross,[12/] the same amount of barium chloride (0.3 gram) was used for both 10- and 20-mm. cells, for the

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[10/] Sheen, R. T., Kahler, H. L., and Ross, E. M., Turbidimetric Determination of Sulfate in Water: Ind. Eng. Chem., anal. ed., vol. 7, 1935, pp. 262-265.

[11/] See footnote 10.

[12/] See footnote 10.

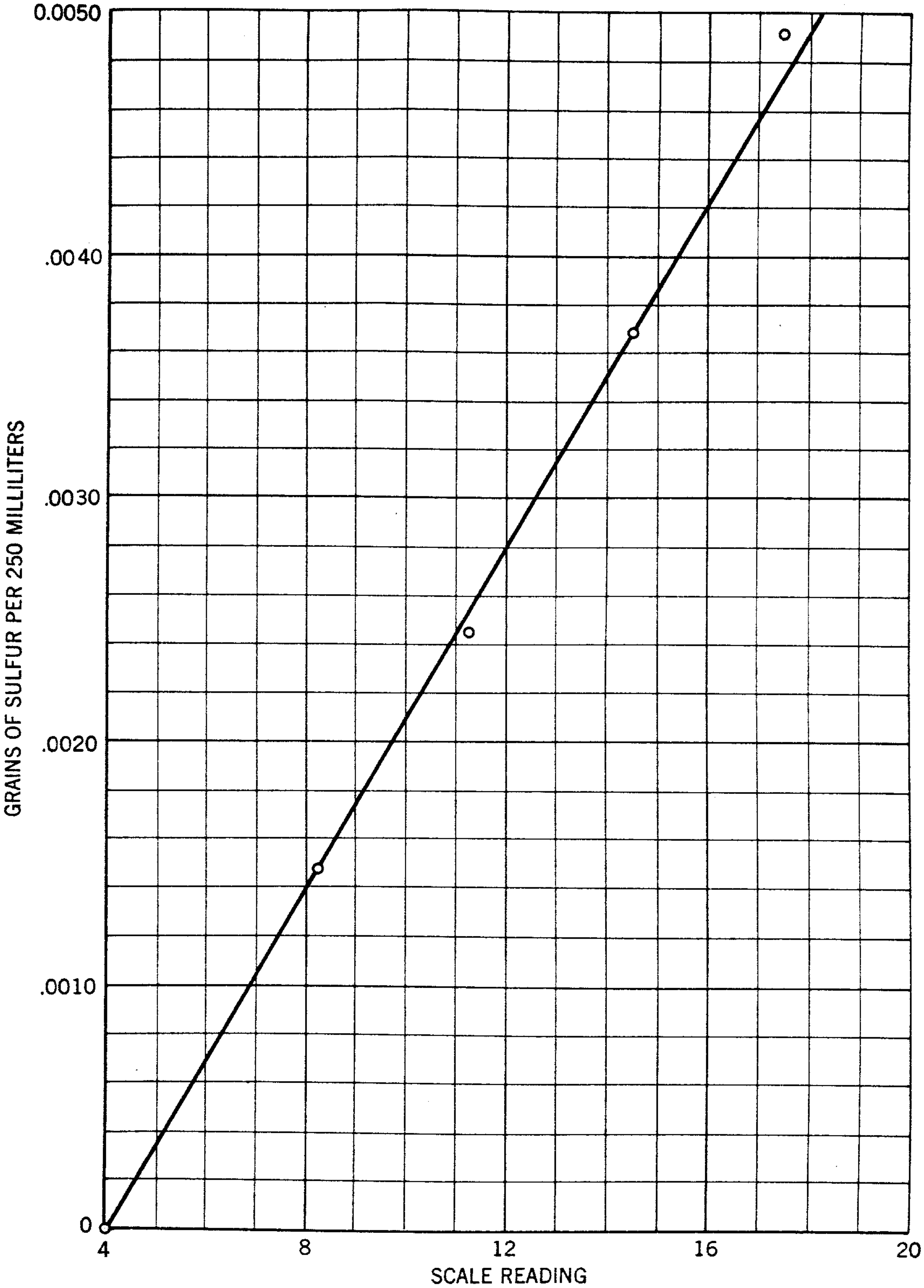

Figure 2. - Turbidimeter calibration, 100-millimeter cell, no filter.

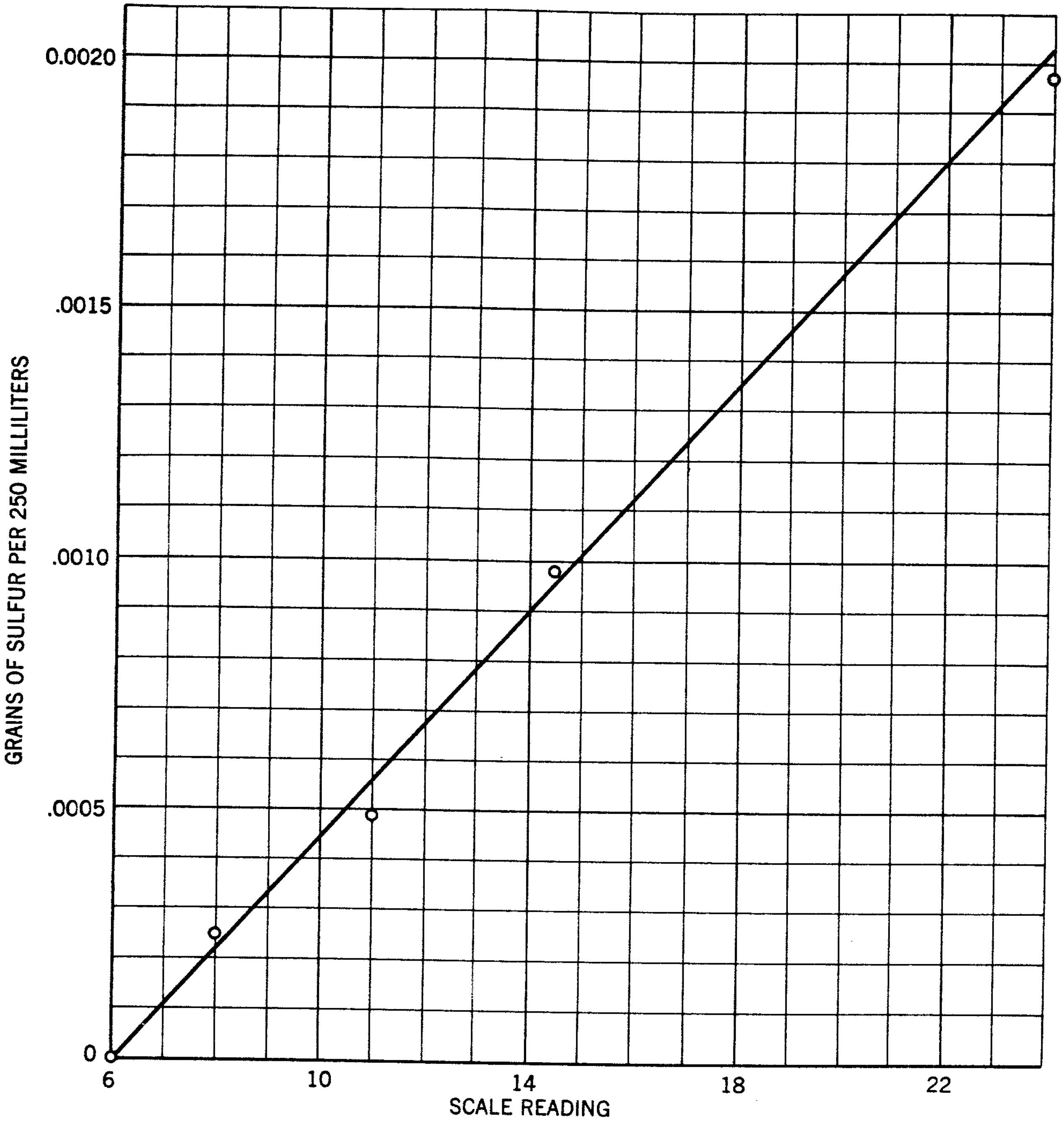

Figure 3. - Turbidimeter calibration, 100-millimeter cell, light filter.

50- and 100-mm. cells the authors' laboratory found it necessary to increase the quantity to 0.6 and 0.9 gram, respectively. Although 0.3 gram exceeds the stoichiometrical amount required for the reaction, the additional barium chloride speeds the formation of turbidity. With slower-forming turbidity, there appears to be a tendency for the barium sulfate to settle to the bottom of the cell before maximum turbidity is developed, giving erratic results.

During calibration of the turbidimeter, it was found necessary to heat the standard solutions to about 150° F. to expel dissolved gases. When this was not done, addition of salt-acid expelled the gases from solution, and bubbles formed at the interface of the plunger and solution, causing high results. This trouble is not experienced during actual analyses, where solutions are boiled as part of the procedure.

The use of a yellow filter in the eyepiece, as first suggested in a letter from the Southern California Gas Laboratory, Los Angeles, Calif., in 1947, appears to facilitate reading the instrument.

As little as 0.001 grain of sulfur (as barium sulfate) per 250 ml. of solution can be detected. This is equivalent to 0.005 grain of sulfur per 100 cu. ft. of gas when only 2 cu. ft. of gas is burned.

Three calibration curves for the 100-ml. cell (figs. 2, 3 and 4) show the turbidimeter-scale range for the lower concentrations of sulfur. To simplify calculations, these are expressed in terms of sulfur per 250 ml. of solution, because the burner absorbent after treatment to oxidize to sulfate is conveniently made up to that volume.

The Bureau's procedure for use of the Betz-Hellige turbidimeter follows:

Reagents

Barium chloride ($BaCl_2.2H_2O$) - 20- to 30-mesh crystals.

Standard salt-acid solution - 240 grams of sodium chloride and 20 cc. of hydrochloric acid (sp. gr. 1.19) per liter. The salt-acid solution must be filtered to zero turbidity. To obtain any noticeable change in the dial reading on the turbidimeter using low-sulfate (less than 1 p.p.m.) samples, it is necessary to add sulfate to the salt-acid solution to correct for the solubility of barium sulfate in water, which is equivalent to 2.85 p.p.m. at 30° C. The amount of sulfate to add to the salt-acid, of course, will depend on the sulfate content of the NaCl and the distilled water used in making up the salt-acid, as well as that of the water used in making up the solution whose sulfate content is to be determined. This can best be determined by running a blank using distilled water and unsulfated salt-acid, and then adding measured amounts of sulfate to the salt-acid until a blank shows a dial reading slightly greater than that read when using the unsulfated salt-acid. Since the ratio of the sample to salt-acid is less (5:1) when the 10-, 20-, and 50-mm. cells are used than the 100-mm. cell (20:3) is used, it was necessary to prepare two different salt-acid solutions and to sulfate each accordingly. In the case of the salt-acid to be used with the former cells, sulfate equivalent to 0.005 gram of barium sulfate was added per liter, whereas with the 100-mm. cell, sulfate equivalent to 0.012 gram of barium sulfate was added per liter. The blank should give a turbidimeter reading equal to or slightly larger than that used for the calibration curves. If the blank is larger, the difference must be subtracted from the sample reading and the corrected reading used to obtain the sulfur content from the calibration curve.

Standard Solutions Used for Calibration Curves

A stock solution using sulfuric acid was made up equivalent to 0.00464 gram of barium sulfate per milliliter. The sulfate content of the stock solution was determined gravimetrically by precipitating with barium chloride and weighing as barium sulfate. To the stock solution was added 12.5 grams of $NaHCO_3$ per liter to simulate the absorber solution used when gas containing organic sulfur compounds is burned. The stock solution was acidified with concentrated HCl and had a pH of 1.5. By proper dilution of this stock solution sample solutions were prepared ranging from 0.464 to 46.4 p.p.m. $BaSO_4$. The pH of the samples ranged from 3.5 to 4.2.

Determination

The following table indicates the amount of sample to be taken, the amount of salt-acid to be used, and the time of reading (minutes after barium chloride addition) for the various sizes of cells:

Cell	Sample, ml.	Salt-acid, ml.	$BaCl_2$, scoops	Time, min.
10	25	5	1 (0.3 gm.)	7
20	50	10	1	9
50	100	20	2 (0.6 gm.)	13
100	200	30	3 (0.9 gm.)	16

Pipette the amount of sample into the cell. Add the required amount of salt-acid. Stir for approximately 15 seconds to insure a homogeneous solution. Add the required number of scoops of barium chloride. Immediately start stopwatch, stirring for exactly 1 minute. Insert the plunger, and take readings every 2 minutes to accustom the eye to changes in the light effect. The actual reading to be used for computations is taken at the time indicated in the foregoing table.

Notes

1. Cells and glassware must be scrupulously clean. Fingerprints, lint, etc., must be removed from the cell. Chamois has been found ideal for this purpose.

2. Care must be taken to avoid scratching the cell walls, since scratches cause a streaky field of different light intensities, contributing to the difficulty of reading. Use a rubber policeman on stirring rod to prevent glass-to-glass contact.

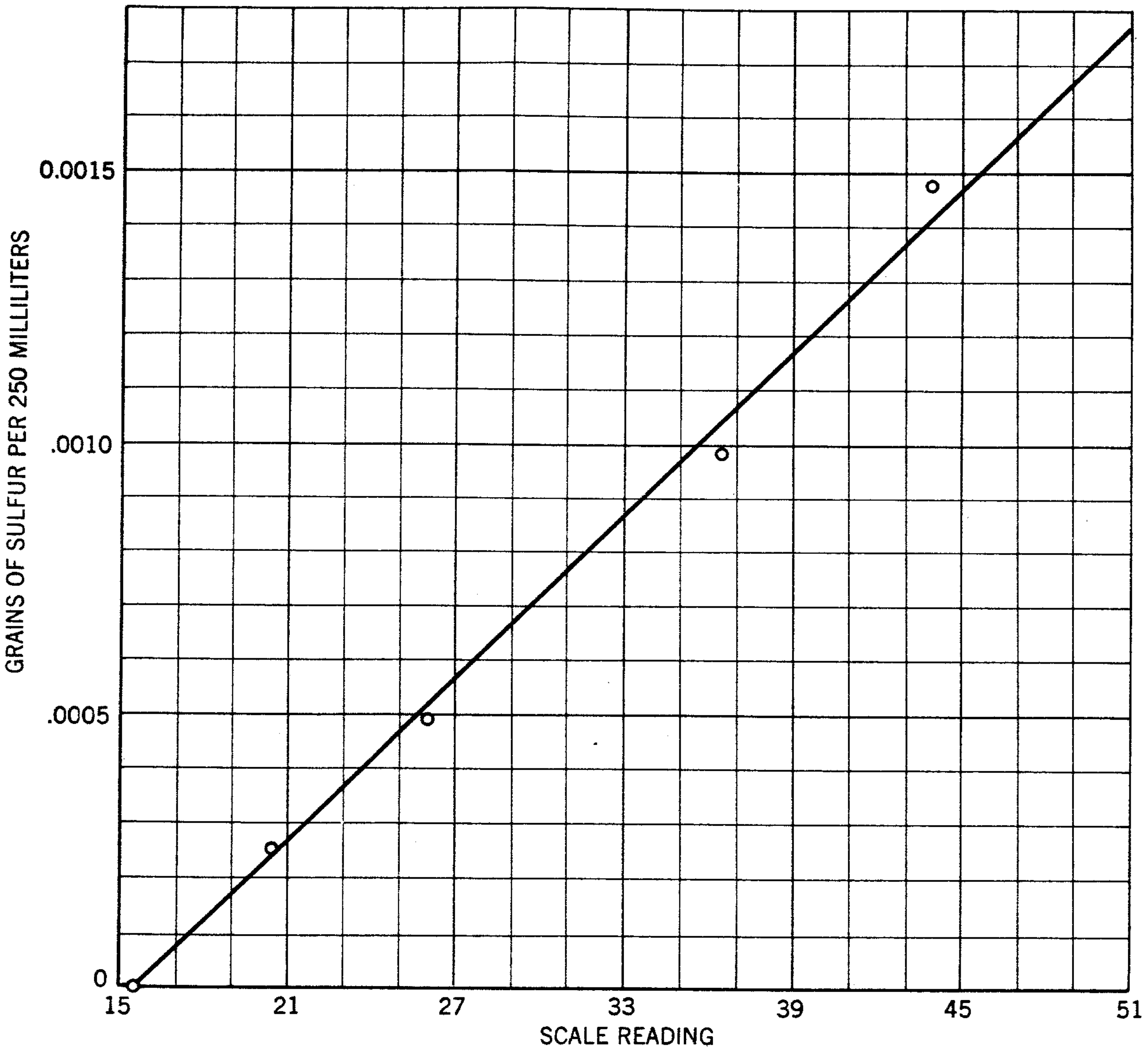

Figure 4. - Turbidimeter calibration, 100-millimeter cell, dark filter.

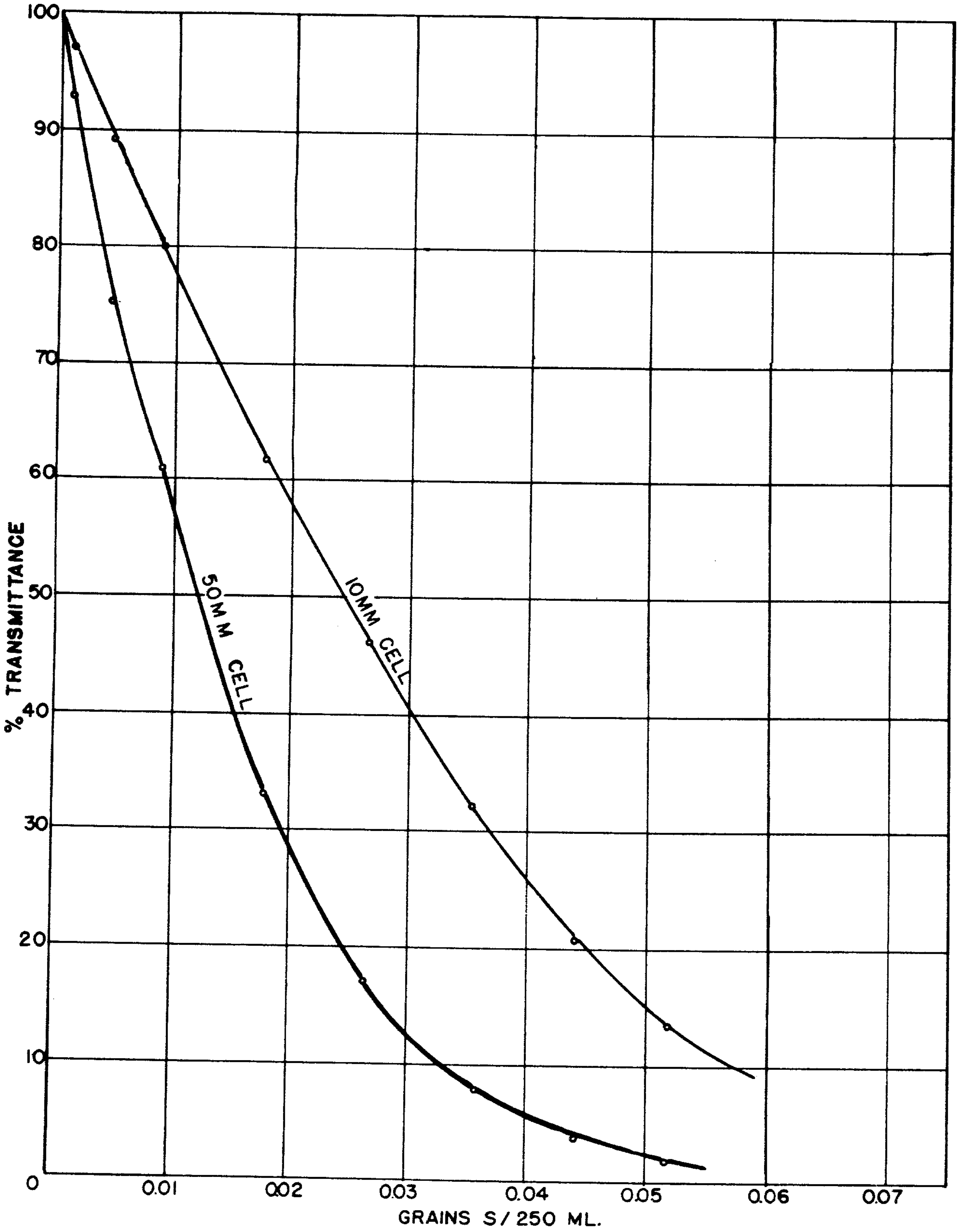

Figure 5. - Calibration curve turbidimetric determination of sulfate using a spectrophotometer λ 340 Mμ.

3. To prevent formation of gas bubbles in the cell, samples should be heated to 150° F., then quickly cooled and used. Heating evolves dissolved gases. This precaution, of course, is not required in the usual analyses where the sample is boiled as a part of regular procedure - for example, to evolve bromine fumes or to concentrate the solution.

4. The sample and salt-acid solution should show no initial turbidity. Standard samples, salt-acid solution, and samples from the burner should always be filtered.

For greatest accuracy in using the Hellige turbidimeter, each analyst should have his own individual calibration curve because of individual differences in making the readings. There is a certain amount of "human error" in judging the exact point of change in light intensity. This error is minimized if each analyst uses his own calibration curve. Even with such errors, the method is considered to be definitely superior to gravimetric determinations when working with very small amounts of barium sulfate.

Spectrophotometric Determination of Barium Sulfate

To eliminate the "human error" in judgment involved in reading the turbidimeter, it was considered desirable to investigate the Beckman spectrophotometer for measuring turbidity of barium sulfate.

For this purpose 20-mm. and 50-mm. cells were used. Figure 5 gives the calibration curves for the cells. A limited amount of work with a 100-mm. cell gave erratic results on extremely low concentrations. For the present, it is preferred to work within the limitations of the 50-mm. cell, concentrating the solution to a greater extent if necessary.

The procedure used consists essentially of pipetting 50 ml. of sample into a 100-ml. beaker, adjusting the temperature to 25° C., adding 10 ml. of the salt-acid solution prepared as described in the procedure for the use of the Hellige Turbidimeter, followed by 1 ml. of 10 percent ammonium nitrate solution as a peptizer. Two Hellige scoops of 20- to 30-mesh barium chloride are added, and the solution is stirred and transferred into the spectrophotometer cell. Using a wave length of 340 millimicrons, readings are taken until the minimum percent transmittance is reached. The sulfur concentration is read from the calibration curve.

Table 5 gives comparisons of the total sulfur in gas determinations by the platinum spiral method and the modified I.G.T. method, using this spectrophotometric measurement of barium sulfate.

TABLE 5. - Comparison of I.G.T.-burner and platinum-spiral methods

Sulfur (as C_4H_4S) per 100 cu. ft., gr.

Platinum spiral	I.G.T. burner
4.91	5.03
4.99	4.99
3.31	3.38
	3.41
3.92	
3.91	4.09
4.14	
	4.10
2.52	
2.56	2.58
2.72	2.80
.971	.992

Miscellaneous Methods for Determining Sulfate

Several methods for determining a sulfate which were found in the literature were investigated for possible application to combustion methods for organic sulfur determination. Among these methods were the following:

Titration using tetrahydroxyquinone indicator.[13][14]

A method depending on precipitation of sulfate with barium chromate and the excess chromate being determined colorimetrically with the use of diphenyl carbazide indicator.[15][16]

A colorimetric method whereby sulfate is precipitated by means of benzidene hydrochloride and the precipitate separated by centrifuging and dissolved in hydrochloric acid followed by diazotization. Color is developed by adding N-(1 Naphthyl) ethylenediamine dihydrochloride.[17]

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[13] Schroeder, W. C., Direct Titration of Sulfate: Ind. Eng. Chem., anal. ed., vol. 5, 1933, pp. 403-406.

[14] Ogg, C. L., Willits, C. O., and Cooper, F. J., Volumetric Determination of Small Amounts of Soluble Sulfate: Ind. Eng. Chem., anal. ed., vol. 20, 1948, pp. 83-85.

[15] Lang, K., A Colorimetric Microchemical Method for the Determination of Sulfur and Sulfate in Biological Fluids: Biochem. Z. & G., vol. 213, 1929, pp. 469-474.

[16] Brubaker, H. W., A Modification of the Modified Winkler Method for the Determination of Sulfate in Water: Jour. Am. Chem. Soc., vol. 34, 1912, p. 284.

[17] Klein, B., Microdetermination of Sulfate: Ind. Eng. Chem., anal. ed., vol. 16, 1944, pp. 536-537.