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# DETERMINATION OF SULPHURIC ANHYDRIDE IN PORTLAND CEMENT BY MEANS OF THE WAGNER TURBIDIMETER

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## ABSTRACT

A turbidimetric method is described for the rapid routine determination of sulphuric anhydride in portland cement by means of the Wagner turbidimeter. The results of several determinations on different brands of cement are tabulated and compared with the results obtained by the standard method.

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## I. INTRODUCTION

For the past 40 years various attempts have been made to develop a satisfactory turbidimetric method for the determination of sulphuric anhydride in portland cement. The Federal specification for portland cement (SS-C-191) and the American Society for Testing Materials standards call for the usual barium sulphate precipitation—a procedure which is entirely satisfactory for umpire determinations but too time-consuming for routine tests. A sufficiently accurate and dependable turbidimetric method would afford considerable saving in time and effort in cement plants and other laboratories making large numbers of control tests.

As early as 1896 Hinds<sup>1</sup> developed a candle turbidimeter for this purpose. Five years later Jackson<sup>2</sup> published a modification of Hinds' method, in which details of technique were more carefully worked out. The Jackson-Hinds method is given without change in Meade's book<sup>3</sup> on portland cement, published in 1926.

Since these first efforts, various investigators have offered improvements in both method and apparatus. Muer<sup>4</sup> improved the precision of his results by using solid barium chloride as the precipitant.

<sup>1</sup> J. I. D. Hinds, *J. Am. Chem. Soc.* **18**, 661 (1896).

<sup>2</sup> D. D. Jackson, *J. Am. Chem. Soc.* **23**, 799 (1901).

<sup>3</sup> Richard K. Meade, *Portland Cement*, p. 466 (1926).

<sup>4</sup> H. F. Muer, *J. Ind. Eng. Chem.* **3**, 553 (1911).

McBride and Weaver,<sup>5</sup> in their work on the determination of sulphur in illuminating gas by means of a turbidimeter, studied the effect of variations in acid concentration and temperature of the solution. In 1931 Parr and Staley<sup>6</sup> developed a turbidimeter which was notable for several mechanical improvements.

All the instruments and methods referred to depend for their accuracy upon the operator's ability to judge the point of disappearance of a candle-flame image or lamp filament, when obscured by a turbid solution. With the development of the photoelectric cell and its application to turbidimetric measurements, it has become possible to eliminate the personal factor in these observations and to increase the accuracy and dependability of the results. In 1933 Wagner<sup>7</sup> constructed a turbidimeter using a photoelectric cell (Weston photronic type) for determining the fineness of portland cement. With this improved instrument a satisfactory technique was evolved for the determination of sulphuric anhydride in cement.

## II. GENERAL CONSIDERATIONS

In addition to a sufficiently sensitive apparatus for measuring turbidity, the success of a nephelometric method for the determination of sulphuric anhydride depends upon the reproduction of approximately the same barium sulphate particle size in suspensions obtained from a given concentration of sulphate ions. The most important variables affecting the particle size of a barium sulphate precipitate obtained from a solution of portland cement are as follows:

1. Acid concentration of the solution.
2. Concentration of other substances in the solution.
3. Temperature of the solution.
4. The crystal size and amount of barium chloride.
5. The manner in which the solution is agitated after the addition of the barium chloride.

Several authors have pointed out that variations in acid concentration have a marked effect on the results obtained, but this factor may be adequately controlled without loss of time by the use of some simple measuring device such as a pipette with the delivery tube cut off near the bulb, to facilitate handling of the acid when a sample is being dissolved. There is reason to believe that variations in the amounts of other substances in the solution affect the particle size of the barium sulphate, but it was found that variations in turbidity, due to differences in composition of the cements studied, were negligible. It is not difficult to maintain the solution within a degree or two of the specified temperature and more accurate control is not necessary. In the method described, 25° C is specified, but the calibration and subsequent determinations could be made at any convenient and arbitrarily chosen temperature between 20 and 30° C.

Probably the most important factor in the reproduction of particle size is the form of the precipitating reagent. Even with less sensitive types of turbidimeters the use of barium chloride solutions was found to be unsatisfactory. Muer recommends the use of barium chloride tablets, which were fairly effective with a visual

<sup>5</sup> R. S. McBride and E. R. Weaver, BS Tech. Pap. **3**, 1 (1913), T20.

<sup>6</sup> S. W. Parr and W. D. Staley, Ind. Eng. Chem. Anal. ed. **3**, no. 1, 66 (1931).

<sup>7</sup> L. A. Wagner, Proc. Am. Soc. Testing Materials, **33**, 11, 553 (1933).

type of instrument, but it was found in this laboratory that they were not suitable for use with the more sensitive type of turbidimeter utilizing a photoelectric cell. Experiments show that approximately 0.5 g of 40- to 80-mesh barium chloride crystals gives satisfactory results. Smaller crystals dissolve too rapidly and cause erratic results like those which accompany the use of barium chloride solutions. Larger crystals can be used but are troublesome to obtain. Furthermore, if a wide range of sizes is used, different bottles of crystals may vary too much in size distribution. Muer has pointed out the variations in turbidity which result from the use of different sizes of crystals and his findings have been confirmed in this laboratory.

The manner in which the solution is stirred after the addition of the barium chloride has a decided effect on the particle size of the precipitate. Violent agitation causes the barium chloride to dissolve too rapidly, and if the solution is stirred too gently, precipitation of the barium sulphate takes place so slowly that the turbidity changes (increases) while the determination is in progress. The best rate of stirring is one which causes nearly all the barium chloride to dissolve during the prescribed 30-second period of stirring. When the barium sulphate precipitation is conducted according to the recommended method, no change (decrease) in turbidity due to crystal growth or settling of the precipitate is indicated by the microammeter in less than 2 minutes after precipitation is complete.

### III. EXPERIMENTAL DETAILS

#### 1. DESCRIPTION OF APPARATUS

A detailed description of the Wagner turbidimeter may be found in the proceedings of the American Society for Testing Materials, volume 33, part II, pages 566-570 (1933), but for convenience a brief description is included here. Referring to figure 1, light source L is a 6-candlepower electric lamp operated by a 6-volt storage battery. A parabolic reflector rigidly attached to the lamp mounting throws a beam of approximately parallel light rays through water cell W<sup>8</sup> and into glass tank T containing a suspension of barium sulphate particles. The light passing through the tank strikes photoelectric cell C (Weston photonic type) and the current generated in the cell is measured with a microammeter. The reading obtained affords a measure of the turbidity of the suspension. R<sub>1</sub> and R<sub>2</sub> are rheostats for regulating the intensity of the light. Filter F (Eastman filter no. 35D has been found suitable), mounted in front of the opening in shield S, reduces the intensity of the light when the tank containing the barium sulphate suspension is not in place, and also serves as a reference standard for light intensity.

The stirring requirement is readily met by agitating the solution with a glass rod which is rotated at about 225 rpm by means of any suitable mechanical device. The rod should be bent about 2 inches from the end so that the tip describes a circle about 1 inch in radius. Its position should be adjusted so that the end of the rod is  $\frac{1}{4}$  to  $\frac{1}{2}$  inch

<sup>8</sup> The function of the water cell is to absorb most of the radiant heat of the light. This cell is a desirable feature of the apparatus when used for the determination of specific surface but it is not essential for determinations of sulphuric anhydride. Movable base B is likewise not needed for these determinations, and is allowed to remain in its lowermost position.

above the bottom of the beaker. A 250-ml beaker is recommended, and it is also to be noted that the same size of beaker must always be used in order that the stirring action be uniform. It is desirable to maintain the speed of the stirring device constant within 25 rpm and at all times within the limits of 200 to 250 rpm. The speed of the stirrer can be readily ascertained by allowing the stirring rod to strike a finger and counting the revolutions over a short interval, such as 15 or 20 seconds.

When the instrument is in use, it is necessary that the lamp in the turbidimeter be maintained at some "standard" brightness. This is accomplished by adjusting the filament temperature by means of the rheostats so that the reading on the microammeter, observed with the colored-glass filter in place but with the solution tank removed, reaches a predetermined value. This value is obtained in the following manner.

Using a sample of cement of known sulphuric anhydride content (determined by the standard gravimetric method), weigh an amount which will furnish exactly 0.100 g of the anhydride. For example, if a sample containing 1.80 percent of sulphuric anhydride is used, 0.5555 g will be required. Dissolve this sample, and precipitate the barium sulphate as directed in the recommended procedure. Transfer to the turbidimeter tank a portion of the solution sufficient to bring its surface well above the light beam. Carefully place the tank against the stops in the instrument. Remove the colored-glass filter and close the cabinet. Adjust the brightness of the lamp so that a reading of approximately 24 microamperes is obtained about 1 minute after the solution is removed from the stirrer and placed in the instrument. Replace the colored-glass filter,<sup>9</sup> remove the tank containing the turbid solution, and observe the reading on the microammeter. This value will then constitute the "standard setting" of the instrument for the particular filter used. This setting is, of course, arbitrary, and the nearest whole-scale division on the meter may be chosen as the standard setting. Subsequently, when the turbidimeter is used, the brightness of the lamp must first be adjusted so that exactly the same predetermined reading is obtained through the colored-glass filter, after the lamp has been allowed to burn for about 5 minutes in order to give the photoelectric cell an opportunity to reach a state of equilibrium.

If a reliable storage battery is used, the reading will remain quite constant for a period sufficient to make several tests. However, it is advisable to check this reading from time to time during a series of determinations and adjust the rheostats in case there has been any change in the brightness of the lamp.

## 2. CALIBRATION OF TURBIDIMETER

To obtain the data for the calibration curve of the turbidimeter, a single cement is used, of which the sulphuric anhydride content has been determined by the method given in Federal Specification SS-C-191. Various weights of the cement are taken in order to obtain the desired amounts of sulphuric anhydride. The weights of sulphuric anhydride are then calculated as percentages based on a

<sup>9</sup> To avoid possible injury to the microammeter, be sure that either the filter or the tank containing a barium sulphate suspension is in the path of the light beam at all times.

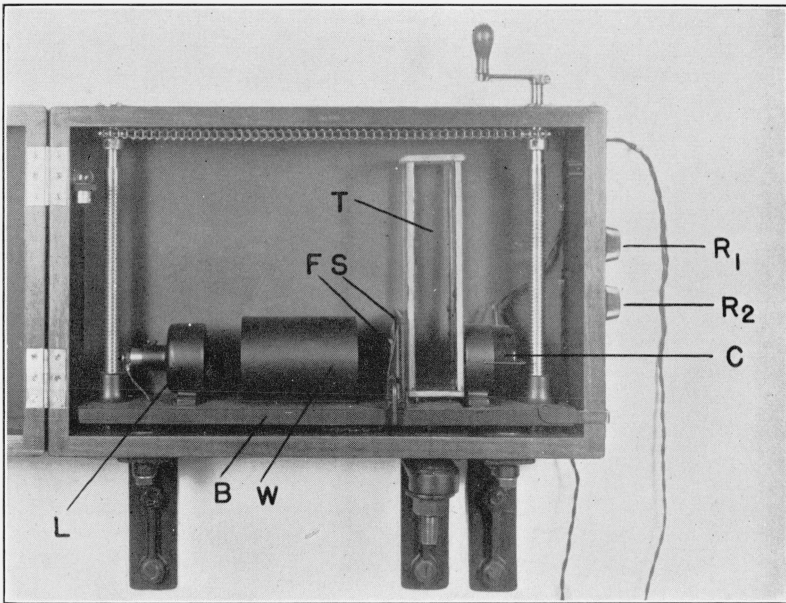


FIGURE 1.—The Wagner turbidimeter.

0.500-g sample (instead of the weight of sample actually taken) and these percentages are plotted against the corresponding microammeter readings. Subsequently, when determinations are made on 0.500-g samples, the percentages of sulphuric anhydride may be read directly from the curve. In this method of calibration, there is

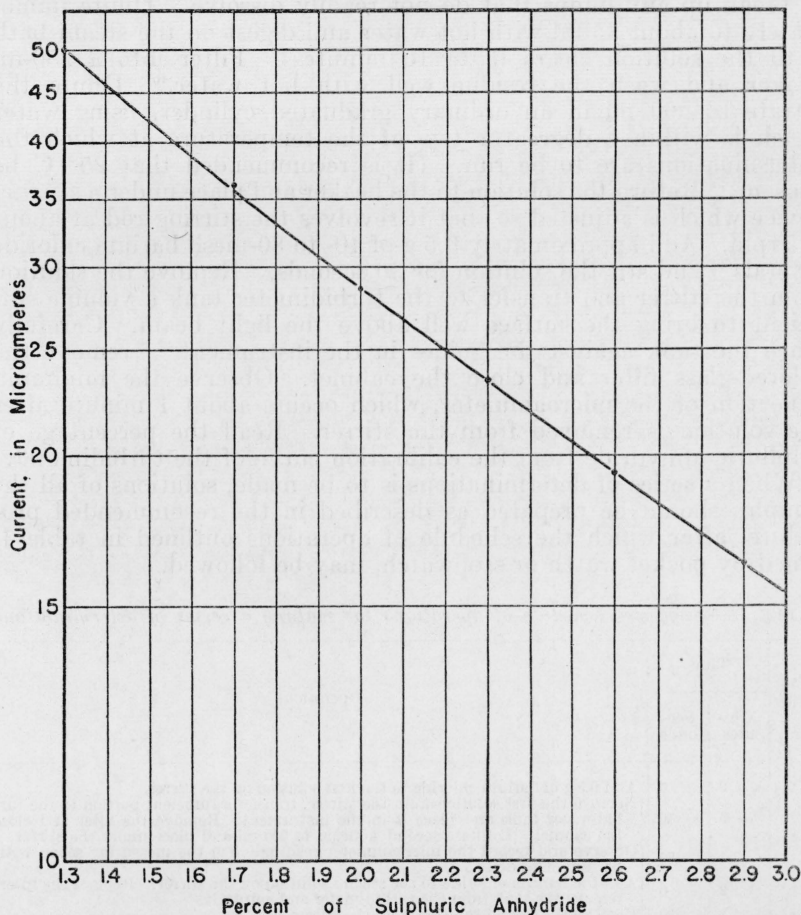


FIGURE 2.—Typical curve showing the relation between microammeter reading and the percentage of sulphuric anhydride in 0.5-g samples.

of course some variation in the amounts of materials in solution (other than sulphates). These variations probably have some effect on the particle size of the barium sulphate, but the error thereby introduced is small as compared with the effects of other variables. The typical curve shown in figure 2 was prepared in the manner described. Each of the points is the average of three determinations. It will be noted that the curve, plotted on semilog paper, very nearly approaches a straight line. Changes in the optical system, such as replacement of the photoelectric cell or the solution tank, will necessitate recalibration of the instrument.

## IV. RECOMMENDED PROCEDURE

To 0.500 g of cement in a 150-ml beaker add 10 ml of cold water (room temperature) and swirl the mixture until the sample is thoroughly dispersed. Continue swirling and add 5 ml of hydrochloric acid (sp gr 1.18). When necessary, a glass rod may be used to break up any lumps that do not readily dissolve. Dilute immediately to about 35 ml with hot water and digest on the steam bath until the solution clears (5 to 10 minutes). Filter into a 250-ml beaker and wash the residue well with hot water.<sup>10</sup> Dilute the filtrate to 200 ml in an ordinary graduated cylinder, using water which is within a degree or two of the temperature at which the determinations are to be run. (It is recommended that 25° C be chosen.) Return the solution to the beaker and place under a stirring device which is adjusted so that it revolves the stirring rod at about 225 rpm. Add approximately 0.5 g of 40- to 80-mesh barium chloride crystals,<sup>11</sup> and stir the solution for 30 seconds. Remove the solution from the stirrer and transfer to the turbidimeter tank a volume sufficient to bring the surface well above the light beam. Carefully place the tank against the guides in the instrument,<sup>12</sup> remove the colored-glass filter and close the cabinet. Observe the minimum deflection of the microammeter, which occurs about 1 minute after the solution is removed from the stirrer. Read the percentage of sulphuric anhydride from the calibration curve of the turbidimeter.

When a series of determinations is to be made, solutions of all the samples should be prepared as described in the recommended procedure, after which the schedule of operations outlined in table 1, timed by pocket watch or stopwatch, may be followed.

TABLE 1.—*Suggested schedule of operations for making a series of determinations*

Series	Time		Operations
	Min-utes	Sec-onds	
A.....	0	0	Add 0.5 g of barium chloride to the first solution on the stirrer.
B.....	0	30	Remove the first solution from the stirrer, transfer a sufficient portion to the turbidimeter tank and place it in the instrument. Remove the filter and close the cabinet. Dilute a second solution to 200 ml and place under the stirrer.
C.....	1	30	Observe and record the microammeter reading. Fill the measuring scoop with barium chloride (0.5 g).
A1....	2	0	Add the barium chloride to the second solution on the stirrer. Replace the filter, remove the tank from the turbidimeter and empty it.
B1....	2	30	Remove the second solution from the stirrer, etc., etc.

<sup>10</sup> Some cements contain so little insoluble material that this filtration may be omitted if only approximate values are desired.

<sup>11</sup> Barium chloride crystals may be measured with sufficient accuracy by means of a small scoop, which can be readily made from a piece of  $\frac{1}{4}$  inch inside diameter brass tubing about  $\frac{1}{16}$  inch long, attached to a suitable handle. (Volume about 0.022 cu in or 0.35 ml).

<sup>12</sup> Care must be exercised to see that the tank containing the turbid solution is placed in exactly the same position each time.

TABLE 2.—Comparison of gravimetric and turbidimetric results

GRAVIMETRIC RESULTS						
Analyst	Sample					
	1	2	3	4	5	6
	%	%	%	%	%	%
A.....	2.24	1.77	2.44	1.53	2.08	1.35
E.....	2.26	1.78	2.44	1.50	2.08	1.33

TURBIDIMETRIC RESULTS						
A.....	2.27	1.79	2.45	1.56	2.09	1.35
B.....	2.24	1.80	2.43	1.56	2.08	1.36
C.....	2.24	1.82	2.45	1.54	2.05	1.34
D.....	2.26	1.79	2.48	1.53	2.09	1.33

## V. DATA AND DISCUSSION OF RESULTS

The results obtained by several operators on a series of six samples tested in the manner described are given in table 2. The gravimetric figures were obtained by the method given in Federal Specification SS-C-191. The turbidimetric results were obtained in the numerical order given in the table, rather than in the order of increasing sulphuric anhydride content, so that any error due to lag of the photoelectric cell with change in light intensity might be apparent.

It will be noted that the readings can be taken at the rate of one every 2 minutes. A complete determination on a single sample can be made in about 15 minutes. As shown in table 2, the turbidimetric method is accurate to about one part in fifty.

WASHINGTON, April 18, 1936.