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### PHOTOMETRIC METHOD FOR THE QUANTITATIVE DETERMINATION OF LIME AND SULPHURIC ACID.<sup>1</sup>

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Received May 14, 1896.

THE want of a rapid method of determining with a close approximation the amount of lime and sulphuric acid in drinking water led me to the study of the opacity of fine white precipitates suspended in water. I precipitated in weak solutions lime with ammonium oxalate, and sulphuric acid with barium chloride, then measured the height of a column of the liquid containing the precipitate through which the flame of a common candle was just invisible. I expected only a rude approximation, but to my surprise, I found that between certain limits, an accuracy is attainable equal to that of the ordinary volumetric methods.

#### APPARATUS.

The only apparatus needed is a cylinder graduated from the bottom in centimeters and tenths. The cylinder should have a plain polished bottom, like Nessler cylinders, and should have a lip at the top. The one I use was made for me by Eimer and Amend. It is four cm. wide and twenty cm. high. The graduations runs to eighteen cm. This cylinder, however, is not absolutely necessary. A common beaker may be used and the depth of the liquid measured with a small ruler.

<sup>1</sup> The manuscript of this article was sent simultaneously to the Chemical News and to this Journal. Owing to the absence from home of Professor Hinds, his proof was delayed too long to allow of publication of the article in the July issue.

## THE METHOD.

*For Sulphuric Acid.*—To determine the value for sulphuric acid, I used a decinormal solution whose actual strength was one cc. equal to 0.00492 gram sulphuric acid. I took ten cc. of this solution, acidulated it slightly with hydrochloric acid, and diluted it to 200 cc. Of this solution I took forty cc., which contained 0.00984 gram sulphuric acid. To this I added enough solid barium chloride to effect complete precipitation, mixed thoroughly by pouring from beaker to cylinder and back, then measured the depth of the column through which the flame was just invisible. I then added successive portions of ten cc. water, taking the measurement after each addition. The measurement is made as follows: Hold the cylinder some twelve inches above the burning candle; looking downward through the cylinder, pour in the liquid until the image of the flame just disappears, then read the depth of the liquid. By applying the lip of the beaker to the lip of the cylinder, a very gentle stream may be made to flow in. The reading should be made two or three times so as to be sure to read the proper tenth. It is well also to enclose the cylinder in the hand, cutting off the surrounding light, so that the observation may be more accurate.

In this way I obtained the series of determinations given below. The strength of the solutions is expressed in per cent. of sulphuric acid, and is represented by  $y$ . Column 1 gives the number of the solution; column 2 the per cent. of sulphuric acid; columns 3, 4, 5 and 6 give the depth of the liquid in centimeters and tenths for four series of observations; column 7 contains the mean of these depths, expressed also by  $x$ ; column 8 contains the products of these means by the percentage, also represented by  $xy$ .

No.	Per cent. sulphuric acid. $y$ .	cm.	cm.	cm.	cm.	cm. $x$ .	$xy$ .
1.....	0.0246	2.4	2.4	2.4	2.4	2.4	0.0590
2.....	0.0197	3.0	3.0	3.0	3.0	3.0	0.0591
3.....	0.0164	3.6	3.6	3.6	3.5	3.575	0.0586
4.....	0.0140	4.2	4.2	4.2	4.2	4.2	0.0588
5.....	0.0123	4.7	4.7	4.8	4.7	4.75	0.0584
6.....	0.0109	5.3	5.4	5.4	5.3	5.35	0.0583

No.	Per cent. sulphuric acid. <i>y</i> .	cm.	cm.	cm.	cm.	cm. <i>x</i> .	<i>xy</i> .
7.....	0.0098	5.8	5.9	5.9	5.8	5.85	0.0573
8.....	0.0089	6.4	6.4	6.4	6.4	6.4	0.0570
9.....	0.0082	6.9	6.9	6.9	6.9	6.9	0.0566
10.....	0.0067	7.4	7.5	7.5	7.5	7.475	0.0568
11.....	0.0070	8.0	8.0	8.1	8.1	8.05	0.0564
12.....	0.0066	8.6	8.6	8.7	8.7	8.65	0.0570

I found that the continued agitation and dilution of the solutions seemed to increase the opacity, though very slightly. I therefore made another series with solutions more dilute with the following results :

No.	Per cent. sulphuric acid. <i>y</i> .	cm.	cm.	cm.	cm.	cm. <i>x</i> .	<i>xy</i> .
1.....	0.0098	6.1	6.1	6.0	6.1	6.075	0.0595
2.....	0.0089	6.6	6.7	6.6	6.6	6.925	0.0589
3.....	0.0083	7.2	7.3	7.3	7.3	7.275	0.0597
4.....	0.0075	7.9	7.9	7.9	7.9	7.9	0.0592
5.....	0.0070	8.5	8.5	8.4	8.4	8.45	0.0591
6.....	0.0066	9.0	9.1	9.1	9.1	9.075	0.0598
7.....	0.0061	9.6	9.6	9.7	9.7	9.675	0.0590
8.....	0.0058	10.2	10.2	10.2	10.2	10.2	0.0591
9.....	0.0055	10.8	10.8	10.8	10.8	10.8	0.0594
Mean value of <i>xy</i> .....							0.0593
Mean value for <i>xy</i> for first six of first series.....							0.0587
Mean of the two.....							0.0590

We observe that the product *xy*, that is, the number obtained by multiplying the per cent. of sulphuric acid in the solution by the depth of the column through which the flame is just invisible, is a constant. The curve, therefore, made by taking the one as the abscissa and the other as the ordinate is an hyperbola referred to its asymptotes, of which the equation is

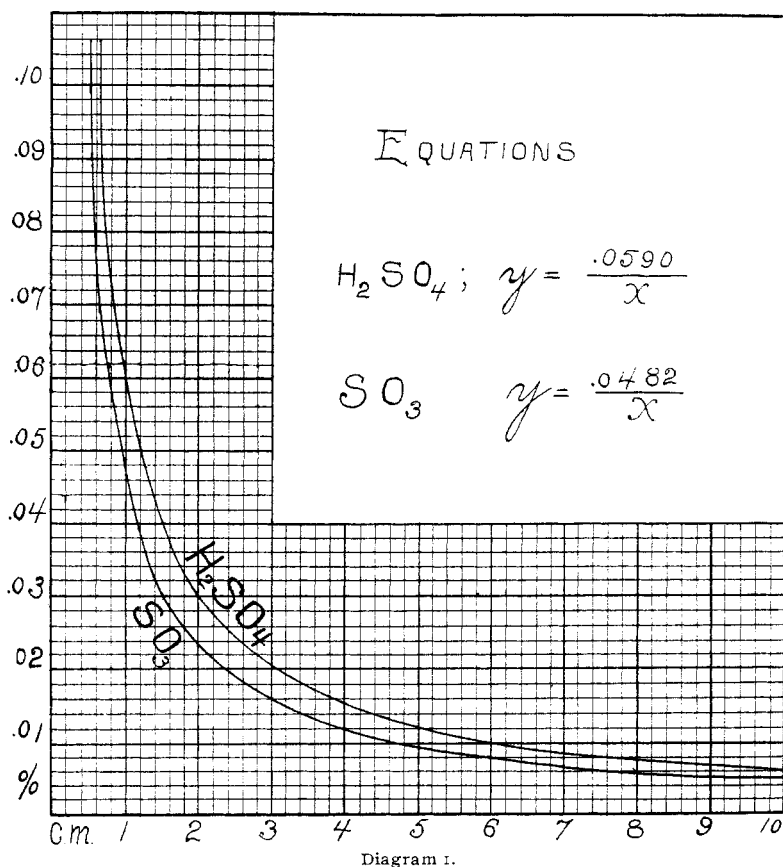
$$xy = 0.0590.$$

This curve is shown in the accompanying diagram. The abscissas are centimeters and the ordinates are 0.01 per cent. to the centimeter.

Solving the equation for *y*, we have

$$y = \frac{0.0590}{x}.$$

To find the amount of sulphuric acid in any solution, observe



the value of  $x$ , divide this into 0.0590, the quotient will be the per cent. of sulphuric acid. Remove the decimal point three places to the right, the result will be parts in 100,000. For example, suppose the depth observed is five cm. The quotient is 0.0118. The solution, therefore, contains 0.0118 per cent. of sulphuric acid, or 11.8 parts in 100,000.

For sulphur trioxide the equation is  $y = \frac{0.0482}{x}$ . This curve is shown in the diagram. In the above example the amount of sulphur trioxide is 0.00965 per cent., or 9.65 parts in 100,000.

## PROBABLE ERROR.

To determine the probable difference between the observed and computed values, we may compare the second set of observations above with the percentages computed from the equation. In the following table the first column contains the observed depths of the liquid, the second gives the actual strength of the solutions used, the third gives the numbers calculated from the equation, the fourth contains the difference, and the fifth the square of the difference between the numbers in the two preceding columns. The difference is represented by  $v$ .

cm.	Per cent. used.	Per cent. computed.	$v$ .	$v^2$ .
6.0	0.0098	0.0098	0.0000	0.00000000
6.6	0.0089	0.0089	0.0000	0.00000000
7.3	0.0082	0.0081	0.0001	0.00000001
7.9	0.0075	0.0075	0.0000	0.00000000
8.5	0.0070	0.0069	0.0001	0.00000001
9.0	0.0066	0.0065	0.0000	0.00000001
9.7	0.0061	0.0061	0.0000	0.00000000
10.2	0.0058	0.0057	0.0001	0.00000001
10.8	0.0055	0.0055	0.0000	0.00000000
			Sum $\sum v^2$	0.00000004

By the method of least squares, the probable error is expressed in the equation

$$r = 0.6745 \sqrt{\frac{\sum v^2}{n-q}},$$

in which  $n$  = the number of observations, in this case 9, and  $q$  the number of constants in the equation, in this case 1. Making the substitutions, the value becomes

$$r = 0.6745 \sqrt{\frac{0.00000004}{8}} = 0.00005.$$

The probable difference then between an observed and a computed value is 0.00005 per cent., or one part in 2,000,000.

*For Calcium Carbonate.*—In the investigation of lime I used a solution of calcium chloride whose strength corresponded exactly to 0.001 gram of calcium carbonate to the cubic centimeter. Ten cc. of this solution was taken and diluted with twenty cc. of water, then enough solid ammonium oxalate was added to pre-

precipitate the whole of the calcium. The solution was then poured into the photometric cylinder and the depth measured as in the case of sulphuric acid. Portions of ten or twenty cc. of water were successively added and the depth observed after each addition. The results are given in the following table. In column 1 is the number of the solution; column 2 shows the per cent. of calcium carbonate; columns 3, 4, 5, 6, and 7 contain the measured depths of the liquid at which the flame became invisible; column 8 contains the means of these depths, and column 9 the product of these means by the per cents. in column 2, represented as before by  $xy$ . The three determinations in the fifth series were made simply as a check. Many other independent determinations were made in order to ascertain whether there was a change of opacity, and whether the precipitation would be different in the weaker solutions. No material difference was found.

No.	Per cent. calcium carbonate.	cm.	cm.	cm.	cm.	cm.	$x$ .	$xy$ .
1.....	0.0333	2.1	2.3	2.3	2.4		2.250	0.0750
2.....	0.0250	2.8	2.9	2.9	2.9		2.875	0.0718
3.....	0.0100	3.5	3.6	3.5	3.5		3.525	0.0705
4.....	0.0167	4.1	4.2	4.1	4.1	4.2	4.14	0.0691
5.....	0.0143	4.7	4.8	4.7	4.7		4.725	0.0676
6.....	0.0125	5.3	5.5	5.3	5.3		5.35	0.0669
7.....	0.0111	6.0	6.1	5.9	6.0		6.0	0.0666
8.....	0.0100	6.6	6.8	6.6	6.7		6.675	0.0668
9.....	0.0091	7.3	7.4	7.3	7.4	7.4	7.36	0.0670
10.....	0.0083	8.0	8.0	8.0	8.1		8.03	0.0666
11.....	0.0077	8.8	8.6	8.6	8.8		8.7	0.0670
12.....	0.0071	9.5	9.3	9.3	9.5		9.4	0.0667
13.....	0.0067	10.2	0.9	9.9	10.1	9.9	10.0	0.0670

Examining the values of  $xy$ , we find that they are not constant. They diminish rapidly at first, then more slowly. The equation is, therefore, not so simple as in the case of sulphuric acid. It appears, however, to be an hyperbola, and we may assume that its equation has the form

$$xy + by = a,$$

in which  $b$  and  $a$  are constants whose values are to be determined. Substituting the values of  $x$  and  $y$  from the above table,

we obtain thirteen observation equations. The values of  $a$  and  $b$  are then found according to the method of least squares by forming and solving the two sets of normal equations. The first set will be the same as the observation equations; the second set is obtained by multiplying each equation by its coefficient of  $b$ . These equations are as follows:

$0.0750 + 0.0333 b = a$	$0.002500 + 0.001111 b = 0.0333 a$
$0.0718 + 0.0250 b = a$	$0.001795 + 0.000625 b = 0.0250 a$
$0.0705 + 0.0200 b = a$	$0.001410 + 0.000400 b = 0.0200 a$
$0.0691 + 0.0167 b = a$	$0.001151 + 0.000271 b = 0.0167 a$
$0.0676 + 0.0143 b = a$	$0.000967 + 0.000204 b = 0.0143 a$
$0.0669 + 0.0125 b = a$	$0.000836 + 0.000156 b = 0.0125 a$
$0.0666 + 0.0111 b = a$	$0.000740 + 0.000124 b = 0.0111 a$
$0.0668 + 0.0100 b = a$	$0.000668 + 0.000100 b = 0.0100 a$
$0.0670 + 0.0091 b = a$	$0.000610 + 0.000083 b = 0.0091 a$
$0.0666 + 0.0083 b = a$	$0.000553 + 0.000069 b = 0.0083 a$
$0.0670 + 0.0077 b = a$	$0.000516 + 0.000059 b = 0.0077 a$
$0.0667 + 0.0071 b = a$	$0.000474 + 0.000050 b = 0.0071 a$
$0.0670 + 0.0067 b = a$	$0.000449 + 0.000045 b = 0.0067 a$

Adding the equations together, we have

$$0.8886 + 0.1818b = 13a. \quad 0.012668 + 0.003304b = 0.1818a.$$

Dividing by the coefficient of  $a$  and eliminating, we have

$$a = 0.0642 \qquad b = -0.3$$

The required equation is therefore

$$xy - 0.3 b = 0.0642,$$

or, solving for  $y$

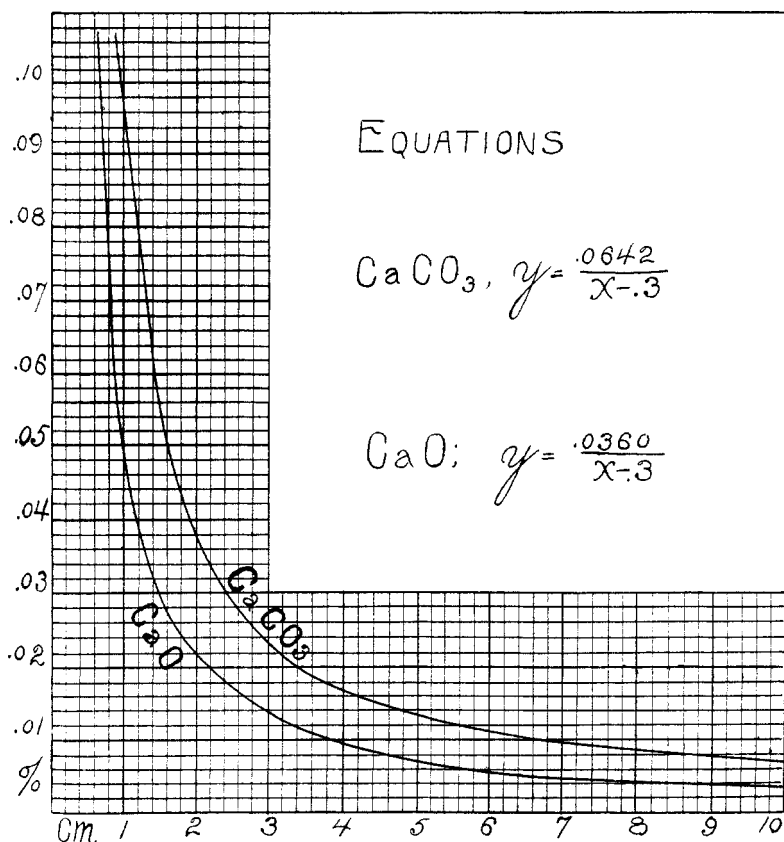
$$y = \frac{0.0642}{x - 0.3}.$$

For the per cent of CaO the equation is

$$y = \frac{0.0360}{x - 0.3}.$$

This is the equation of an hyperbola referred to one of its asymptotes as the axis of  $x$  and to an axis of  $y$  three-tenths cm. to the left of the other asymptote. The abscissas are centimeters and the ordinates are 0.01 per cent. to the cm. The curves are shown in the accompanying diagram.

As an example, let us suppose that the observed depth is four and seven-tenths cm. Subtract 0.3 and divide 0.0642 by the



remainder. The quotient 0.0146 is the per cent. of calcium carbonate. Dividing this by 1000 we have 14.6 parts to the 100,000.

#### PROBABLE ERROR.

To determine the probable error of an observation we may compare as before the numbers found by observation with those computed from the equation, as follows :

$x$ .	Strength used.	Strength computed.	$v$ .	$\frac{1}{2}$ .
2.9	0.0250	0.0247	0.0003	0.00000009
3.5	0.0200	0.0201	0.0001	0.00000001
4.1	0.0167	0.0170	0.0003	0.00000009

<i>x</i> .	Strength. used.	Strength. computed.	<i>v</i> .	<i>v</i> <sup>2</sup> .
4.7	0.0143	0.0146	0.0003	0.00000009
5.35	0.0125	0.0127	0.0002	0.00000004
6.0	0.0111	0.0112	0.0001	0.00000001
6.7	0.0100	0.0100	0.0000	0.00000000
7.4	0.0091	0.0091	0.0000	0.00000000
8.0	0.0083	0.0085	0.0002	0.00000004
8.7	0.0077	0.0077	0.0000	0.00000000
9.4	0.0071	0.0071	0.0000	0.00000000
10.0	0.0067	0.0066	0.0001	0.00000001
Sum $\sum v^2$				0.00000038

Using the same value for error as before, in which in this case *n*, the number of observations, is 12, and *q*, the number of constants in the equation is 2, we have

$$r = 0.6745 \sqrt{\frac{0.00000038}{12-2}} = 0.00013 \text{ per cent.}$$

That is, the probable difference between an observed and computed strength of a solution is 0.00013 per cent., or thirteen parts in ten million.

#### SOURCES OF ERROR.

The principal sources of error in this method are two. In the first place a light of constant intensity should be used. It makes but little difference what the light is, so it is the same as that with which the constant in the equation is determined. I employed the flame of an ordinary candle as the most convenient. A brighter and steadier light would give better results. Any change of light will of course change the constants.

The second source of error is the personal equation. Each individual can determine this for himself. The error dependent upon the eye can be almost eliminated by using it in the usual way, that is with or without glasses.

Any one can obtain the constants for himself by making a few determination with solutions of known strength. The best strength to use is that between 0.01 and 0.03 per cent. Great care must be used in measuring. If ten cc. of a decinormal solution are taken, a difference of one drop in the measurement may make an error ten times as great as that involved in the method.

## PRACTICAL APPLICATION.

I have so far used the method and tested it only in sanitary water analysis and in the analysis of urine. To the water analyst it will be of great value. It gives the lime and sulphuric acid with almost the accuracy of the gravimetric method. It is more accurate than the soap test and is but slightly affected by the presence of magnesium salts.

For determining the sulphuric acid in urine I have found it quite satisfactory. The urine has to be diluted with nine volumes of water and then the color does not sensibly affect the determination.

I see no reason why this method may not be successfully used with all fine white precipitates. It is not suitable for precipitates that settle rapidly or gather quickly into flakes. Whether colored precipitates may be determined in this way is still to be investigated.

I desire to acknowledge obligation to Professor A. H. Buchanan for assistance in determining the equations and probable errors.

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[CONTRIBUTIONS FROM JOHN HARRISON LABORATORY OF CHEMISTRY.  
NO. 12.]

## THE SEPARATION OF TRIMETHYLAMINE FROM AMMONIA.

BY HERMANN FLECK.

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THE quantitative estimation of trimethylamine in presence of ammonia is, I believe not mentioned in the literature, although a number of publications have appeared in which the detection of trimethylamine, in presence of ammonia, by means of the different solubilities of their hydrochlorides in absolute alcohol, has been successfully carried out.

Dessaignes<sup>1</sup> prepared and analyzed with good results the platinum double salt of trimethylamine, by conducting the mixture of ammonia and trimethylamine vapors into hydrochloric acid, evaporating to dryness, extracting with absolute alcohol, precipitating with platinic chloride and recrystallizing the precipitate formed several times from hot water.

<sup>1</sup> *Ann. Chem. (Liebig)*, 81, 106.