# LIME AND SULPHURIC ACID BY THE PHOTOMETRIC METHOD.

By J. I. D. Hinds.

Received March 30, 1900.

IN this Journal, **18**, 661, I gave the results of some investigations looking to the rapid determination of lime and sulphuric acid by means of the opacity of the precipitates produced in the usual way. Since then I have had occasion to make frequent tests of the accuracy of the method and am able to give some interesting results.

The only apparatus needed is the photometric cylinder made of glass. It is 3.5 centimeters wide and 20 centimeters high, and is graduated in centimeters and millimeters from the inside of the bottom for the convenient reading of the depth of the liquid in the cylinder. It is used with an ordinary sperm or wax candle. The cylinder is held over the lighted candle and the water containing the precipitate is poured into the cylinder until the image of the flame just disappears. The depth is read and the per cent. is calculated from the equation or read from a table. The lime is precipitated with solid calcium oxalate and the sulphuric acid with solid barium chloride. The equations used are as follows :

$$\text{For } CaCO_3,\ y = \frac{0.0642}{x - 0.3}; \qquad \text{For } CaO,\ y = \frac{0.0360}{x - 0.3};$$

$$\text{For } H_2SO_4,\ y = \frac{0.0590}{x}; \qquad \text{For } SO_3,\ y = \frac{0.0482}{x};$$

in which $x$ is the reading of the cylinder and $y$ the per cent. sought. For the details of the method, see the article above referred to. A table computed from these equations is appended to this article.

Near the university building in Lebanon is a bored well yielding a limestone water, analysis of which shows that it contains among other things

| | | | | |
|---|---|---|---|---|
| Calcium carbonate about | 16.00 | parts | in | 100,000 |
| Magnesium " " | 13.00 | " | " | 100,000 |
| Magnesium sulphate " | 16.00 | " | " | 100,000 |
| Total solids | 60.80 | " | " | 100,000 |

I made a series of photometric and gravimetric determinations of the lime and sulphuric acid in this water from day to day, with the following results:

Calcium carbonate—parts in 100,000.

| | 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|---|---|---|---|---|---|---|---|
| Photometric | 16.5 | 15.7 | 15.7 | 16.5 | 15.7 | 22.2 | 19.5 |
| Gravimetric | 16.4 | 16.0 | 15.5 | 16.0 | 15.5 | 22.4 | 19.0 |
| Difference | 0.1 | 0.3 | 0.2 | 0.5 | 0.2 | 0.2 | 0.5 |

Sulphuric acid—parts in 100,000.

| | 1. | 2. | 3. | 4. | 5. |
|---|---|---|---|---|---|
| Photometric | 13.1 | 11.8 | 5.7 | 7.9 | 4.9 |
| Gravimetric | 13.2 | 11.4 | 5.4 | 7.2 | 4.7 |
| Difference | 0.1 | 0.4 | 0.3 | 0.7 | 0.2 |

These differences, omitting the decimal point, mean parts in a million of the water and are a reasonably small fraction of the total amount present. For sanitary and technical purposes the photometric determinations are just as good as those made in the regular way. When we consider that one of these determinations can be made in five minutes and that the method is adapted to many other substances, it seems to be worthy of the attention and careful investigation of chemists. It is much more accurate than many of the approximate methods now in use and requires no previous preparation in the way of standard solutions.

I have found the method practicable in the determination of the lime in carbonates. I give one example. A sample of clayey limestone containing 16.14 per cent. of calcium carbonate gave by this method 16.46 per cent. The determination was made as follows: Dissolved 0.1081 gram of the limestone in hydrochloric acid with a few drops of nitric acid, evaporated to dryness in a porcelain dish over a free flame, added water with a little hydrochloric acid, filtered, neutralized with ammonia, made up to 150 cc., then tested in the usual way. The reading in the cylinder was 6.0 cm. Substituting this for $x$ in the equation we find the solution to contain 0.0112 per cent. of calcium carbonate. The calculation is then made as follows:

100 cc. contain 0.0112 gram $CaCO_3$.
150 " " 0.0178 " "

0.1081 gram of the sample contains 0.0178 gram $CaCO_3$, or

16.46 per cent. The whole operation can be performed within a half hour.

The determination of sulphuric acid in urine is very easy and rapid. Five or ten cc. of the urine are measured from a burette or pipette, made slightly acid with hydrochloric acid, and diluted to 100 cc. Barium chloride is added and the reading taken. Two trials with a urine diluted from 10 to 100 cc. gave the same reading; *viz.*, 3.0 cm. This corresponds to 0.0197 per cent. $H_2SO_4$. Multiplying by 10 we have 0.197 as the per cent. of $H_2SO_4$ in the urine.

To save the trouble and labor of computation I have prepared the accompanying table from which the percentages can be directly taken as soon as the reading is made.

TABLE FOR PHOTOMETRIC DETERMINATION OF LIME AND SULPHURIC ACID.

$y$ equals the per cent. desired, and $x$ is the reading of cylinder in centimeters. For parts in 100,000 remove the decimal point three places to the right.

| $x$. | Per cent. $CaCO_3$. $y=\frac{0.0642}{x-0.3}$. | Per cent. CaO. $y=\frac{0.0360}{x-0.3}$. | Per cent. $H_2SO_4$. $y=\frac{0.0590}{x}$. | Per cent. $SO_3$, $y=\frac{0.0482}{x}$. |
|---|---|---|---|---|
| 1.0 | 0.0917 | 0.0514 | 0.0590 | 0.0482 |
| 1.1 | 0.0802 | 0.0450 | 0.0536 | 0.0438 |
| 1.2 | 0.0713 | 0.0400 | 0.0492 | 0.0402 |
| 1.3 | 0.0642 | 0.0360 | 0.0454 | 0.0371 |
| 1.4 | 0.0583 | 0.0327 | 0.0421 | 0.0344 |
| 1.5 | 0.0534 | 0.0300 | 0.0393 | 0.0322 |
| 1.6 | 0.0494 | 0.0277 | 0.0370 | 0.0301 |
| 1.7 | 0.0456 | 0.0257 | 0.0347 | 0.0283 |
| 1.8 | 0.0428 | 0.0240 | 0.0328 | 0.0268 |
| 1.9 | 0.0401 | 0.0225 | 0.0311 | 0.0254 |
| 2.0 | 0.0377 | 0.0212 | 0.0295 | 0.0241 |
| 2.1 | 0.0356 | 0.0201 | 0.0281 | 0.0230 |
| 2.2 | 0.0338 | 0.0190 | 0.0268 | 0.0219 |
| 2.3 | 0.0321 | 0.0180 | 0.0257 | 0.0210 |
| 2.4 | 0.0306 | 0.0172 | 0.0246 | 0.0201 |
| 2.5 | 0.0292 | 0.0164 | 0.0236 | 0.0193 |
| 2.6 | 0.0279 | 0.0156 | 0.0227 | 0.0185 |
| 2.7 | 0.0268 | 0.0150 | 0.0218 | 0.0179 |
| 2.8 | 0.0257 | 0.0144 | 0.0211 | 0.0172 |
| 2.9 | 0.0247 | 0.0138 | 0.0203 | 0.0166 |
| 3.0 | 0.0238 | 0.0133 | 0.0197 | 0.0161 |
| 3.1 | 0.0229 | 0.0129 | 0.0190 | 0.0156 |
| 3.2 | 0.0221 | 0.0124 | 0.0184 | 0.0151 |

| $x$. | Per cent. $CaCO_3$. $y = \frac{0.0642}{x - 0.3}$. | Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$. | Per cent. $H_2SO_4$. $y = \frac{0.0590}{x}$. | Per cent. $SO_3$. $y = \frac{0.0482}{x}$. |
|---|---|---|---|---|
| 3.3 | 0.0214 | 0.0120 | 0.0179 | 0.0146 |
| 3.4 | 0.0207 | 0.0116 | 0.0174 | 0.0142 |
| 3.5 | 0.0201 | 0.0112 | 0.0169 | 0.0138 |
| 3.6 | 0.0195 | 0.0109 | 0.0164 | 0.0134 |
| 3.7 | 0.0189 | 0.0106 | 0.0159 | 0.0130 |
| 3.8 | 0.0183 | 0.0103 | 0.0155 | 0.0127 |
| 3.9 | 0.0178 | 0.0100 | 0.0151 | 0.0124 |
| 4.0 | 0.0173 | 0.0097 | 0.0147 | 0.0121 |
| 4.1 | 0.0169 | 0.00947 | 0.0144 | 0.0118 |
| 4.2 | 0.0165 | 0.00923 | 0.0141 | 0.0115 |
| 4.3 | 0.0161 | 0.00900 | 0.0137 | 0.0112 |
| 4.4 | 0.0157 | 0.00878 | 0.0134 | 0.0110 |
| 4.5 | 0.0153 | 0.00857 | 0.0131 | 0.0107 |
| 4.6 | 0.0149 | 0.00837 | 0.0128 | 0.0105 |
| 4.7 | 0.0146 | 0.00818 | 0.0125 | 0.0103 |
| 4.8 | 0.0143 | 0.00800 | 0.0123 | 0.0101 |
| 4.9 | 0.0140 | 0.00782 | 0.0120 | 0.00983 |
| 5.0 | 0.0137 | 0.00766 | 0.0118 | 0.00964 |
| 5.1 | 0.0134 | 0.00750 | 0.0116 | 0.00945 |
| 5.2 | 0.0131 | 0.00735 | 0.0113 | 0.00927 |
| 5.3 | 0.0128 | 0.00720 | 0.0111 | 0.00909 |
| 5.4 | 0.0126 | 0.00706 | 0.0109 | 0.00992 |
| 5.5 | 0.0123 | 0.00692 | 0.0107 | 0.00876 |
| 5.6 | 0.0121 | 0.00679 | 0.0105 | 0.00861 |
| 5.7 | 0.0119 | 0.00667 | 0.0104 | 0.00845 |
| 5.8 | 0.0117 | 0.00654 | 0.0102 | 0.00831 |
| 5.9 | 0.0115 | 0.00643 | 0.0100 | 0.00817 |
| 6.0 | 0.0113 | 0.00632 | 0.00983 | 0.00804 |
| 6.1 | 0.0111 | 0.00621 | 0.00967 | 0.00790 |
| 6.2 | 0.0109 | 0.00610 | 0.00952 | 0.00777 |
| 6.3 | 0.0107 | 0.00600 | 0.00937 | 0.00765 |
| 6.4 | 0.0105 | 0.00590 | 0.00922 | 0.00753 |
| 6.5 | 0.0104 | 0.00580 | 0.00908 | 0.00742 |
| 6.6 | 0.0102 | 0.00571 | 0.00894 | 0.00730 |
| 6.7 | 0.01003 | 0.00562 | 0.00881 | 0.00719 |
| 6.8 | 0.00988 | 0.00554 | 0.00868 | 0.00709 |
| 6.9 | 0.00973 | 0.00545 | 0.00855 | 0.00698 |
| 7.0 | 0.00958 | 0.00537 | 0.00843 | 0.00689 |
| 7.1 | 0.00944 | 0.00529 | 0.00831 | 0.00679 |
| 7.2 | 0.00930 | 0.00522 | 0.00820 | 0.00669 |
| 7.3 | 0.00917 | 0.00514 | 0.00808 | 0.00660 |
| 7.4 | 0.00904 | 0.00507 | 0.00797 | 0.00651 |
| 7.5 | 0.00892 | 0.00500 | 0.00787 | 0.00642 |
| 7.6 | 0.00879 | 0.00493 | 0.00776 | 0.00634 |

| $x$. | Per cent. $CaCO_3$. $y = \frac{0.0642}{x - 0.3}$. | Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$. | Per cent. $H_2SO_4$. $y = \frac{0.0590}{x}$. | Per cent. $SO_3$. $y = \frac{0.0482}{x}$. |
|---|---|---|---|---|
| 7.7 | 0.00867 | 0.00486 | 0.00766 | 0.00626 |
| 7.8 | 0.00856 | 0.00480 | 0.00756 | 0.00618 |
| 7.9 | 0.00845 | 0.00474 | 0.00747 | 0.00610 |
| 8.0 | 0.00834 | 0.00468 | 0.00737 | 0.00602 |
| 8.1 | 0.00823 | 0.00462 | 0.00728 | 0.00595 |
| 8.2 | 0.00813 | 0.00456 | 0.00720 | 0.00588 |
| 8.3 | 0.00802 | 0.00450 | 0.00711 | 0.00581 |
| 8.4 | 0.00792 | 0.00444 | 0.00702 | 0.00574 |
| 8.5 | 0.00783 | 0.00439 | 0.00694 | 0.00567 |
| 8.6 | 0.00773 | 0.00434 | 0.00686 | 0.00560 |
| 8.7 | 0.00764 | 0.00429 | 0.00678 | 0.00554 |
| 8.8 | 0.00755 | 0.00424 | 0.00670 | 0.00548 |
| 8.9 | 0.00746 | 0.00419 | 0.00663 | 0.00541 |
| 9.0 | 0.00738 | 0.00414 | 0.00655 | 0.00536 |
| 9.1 | 0.00730 | 0.00409 | 0.00648 | 0.00530 |
| 9.2 | 0.00721 | 0.00404 | 0.00641 | 0.00524 |
| 9.3 | 0.00713 | 0.00400 | 0.00634 | 0.00518 |
| 9.4 | 0.00705 | 0.00396 | 0.00628 | 0.00513 |
| 9.5 | 0.00698 | 0.00391 | 0.00621 | 0.00507 |
| 9.6 | 0.00690 | 0.00387 | 0.00615 | 0.00502 |
| 9.7 | 0.00683 | 0.00383 | 0.00608 | 0.00497 |
| 9.8 | 0.00676 | 0.00379 | 0.00602 | 0.00492 |
| 9.9 | 0.00669 | 0.00375 | 0.00596 | 0.00487 |
| 10.0 | 0.00662 | 0.00371 | 0.00590 | 0.00482 |
| 10.1 | 0.00655 | 0.00367 | 0.00584 | 0.00477 |
| 10.2 | 0.00648 | 0.00364 | 0.00578 | 0.00473 |
| 10.3 | 0.00642 | 0.00360 | 0.00573 | 0.00468 |
| 10.4 | 0.00636 | 0.00357 | 0.00567 | 0.00463 |
| 10.5 | 0.00629 | 0.00353 | 0.00562 | 0.00459 |
| 10.6 | 0.00623 | 0.00350 | 0.00557 | 0.00455 |
| 10.7 | 0.00617 | 0.00346 | 0.00551 | 0.00451 |
| 10.8 | 0.00611 | 0.00343 | 0.00546 | 0.00447 |
| 10.9 | 0.00606 | 0.00340 | 0.00541 | 0.00442 |
| 11.0 | 0.00600 | 0.00336 | 0.00536 | 0.00438 |
| 11.1 | 0.00594 | 0.00333 | 0.00532 | 0.00434 |
| 11.2 | 0.00589 | 0.00330 | 0.00528 | 0.00430 |
| 11.3 | 0.00584 | 0.00327 | 0.00523 | 0.00426 |
| 11.4 | 0.00578 | 0.00324 | 0.00518 | 0.00423 |
| 11.5 | 0.00573 | 0.00321 | 0.00513 | 0.00419 |
| 11.6 | 0.00568 | 0.00318 | 0.00508 | 0.00415 |
| 11.7 | 0.00563 | 0.00316 | 0.00504 | 0.00412 |
| 11.8 | 0.00558 | 0.00313 | 0.00500 | 0.00408 |
| 11.9 | 0.00553 | 0.00310 | 0.00496 | 0.00405 |
| 12.0 | 0.00548 | 0.00308 | 0.00492 | 0.00401 |

| $x$. | Per cent. $CaCO_3$. $y = \frac{0.0642}{x - 0.3}$. | Per cent. CaO. $y = \frac{0.0360}{x - 0.3}$. | Per cent. $H_2SO_4$. $y = \frac{0.0590}{x}$. | Per cent. $SO_3$. $y = \frac{0.0482}{x}$. |
|---|---|---|---|---|
| 12.1 | 0.00543 | 0.00305 | 0.00488 | 0.00398 |
| 12.2 | 0.00539 | 0.00303 | 0.00484 | 0.00395 |
| 12.3 | 0.00535 | 0.00300 | 0.00480 | 0.00392 |
| 12.4 | 0.00531 | 0.00298 | 0.00476 | 0.00389 |
| 12.5 | 0.00526 | 0.00295 | 0.00472 | 0.00386 |
| 12.6 | 0.00522 | 0.00293 | 0.00468 | 0.00383 |
| 12.7 | 0.00517 | 0.00290 | 0.00465 | 0.00380 |
| 12.8 | 0.00513 | 0.00288 | 0.00461 | 0.00377 |
| 12.9 | 0.00509 | 0.00285 | 0.00457 | 0.00374 |
| 13.0 | 0.00505 | 0.00283 | 0.00454 | 0.00371 |
| 13.2 | 0.00498 | 0.00279 | 0.00447 | 0.00364 |
| 13.4 | 0.00490 | 0.00275 | 0.00440 | 0.00359 |
| 13.6 | 0.00483 | 0.00271 | 0.00434 | 0.00354 |
| 13.8 | 0.00476 | 0.00267 | 0.00427 | 0.00349 |
| 14.0 | 0.00469 | 0.00263 | 0.00421 | 0.00344 |
| 14.2 | 0.00462 | 0.00259 | 0.00415 | 0.00339 |
| 14.4 | 0.00455 | 0.00255 | 0.00410 | 0.00335 |
| 14.6 | 0.00449 | 0.00251 | 0.00404 | 0.00330 |
| 14.8 | 0.00443 | 0.00248 | 0.00399 | 0.00326 |
| 15.0 | 0.00437 | 0.00245 | 0.00393 | 0.00321 |
| 15.5 | 0.00422 | 0.00237 | 0.00381 | 0.00311 |
| 16.0 | 0.00409 | 0.00229 | 0.00369 | 0.00301 |
| 16.5 | 0.00396 | 0.00222 | 0.00358 | 0.00292 |
| 17.0 | 0.00384 | 0.00216 | 0.00347 | 0.00284 |
| 17.5 | 0.00373 | 0.00209 | 0.00337 | 0.00276 |
| 18.0 | 0.00363 | 0.00203 | 0.00328 | 0.00268 |
| 18.5 | 0.00353 | 0.00198 | 0.00319 | 0.00261 |
| 19.0 | 0.00343 | 0.00192 | 0.00311 | 0.00254 |
| 19.5 | 0.00334 | 0.00187 | 0.00303 | 0.00247 |
| 20.0 | 0.00326 | 0.00183 | 0.00295 | 0.00241 |

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[CONTRIBUTIONS FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY, NO. 22.]

# UPON BISMUTH COBALTICYANIDE.

BY J. A. MATHEWS.

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IN a recent article entitled "A Preliminary Study of the Cobalticyanides,"[1] by E. H. Miller and myself, mention was made of bismuth cobalticyanide. It was stated that "the original precipitate seems to be a normal cobalticyanide, but it has not been analyzed and no mention of such a compound is found in the

1 This Journal, 22, 65 (1900).