

consists of both hexose anhydrides and pentose anhydrides; I am not prepared to say whether that would be suitable for paper-making or not; I should think likely not. So that what we arrive at when we try to work from a purely chemical standpoint might be entirely unsuited to a given commercial case.

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## IMPROVEMENTS ON DR. SQUIBB'S VOLUMETRIC METHOD FOR ESTIMATING ACETONE.

BY LYMAN F. KEBLER.

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IN the December<sup>1</sup> number of this Journal Dr. Squibb gave a translation of MM. J. Robineau<sup>2</sup> and G. Rollin's method for estimating acetone, as well as a modification of the process by himself. Both methods consist essentially in mixing an aqueous acetone solution with a strongly alkaline potassium iodide solution and converting the acetone into iodoform by means of a titrated solution of sodium hypochlorite, the end reaction being determined by means of a bicarbonated starch solution.

Dr. Squibb kindly sent me his modification last summer. Prior to that time I had used Messinger's process exclusively. I have not applied Robineau and Rollin's method to any extent, but have studied and worked with Dr. Squibb's modification of the same quite considerably.

The two latter methods will meet with two objections; first, a *pure acetone*, and second, the tedious, time-consuming drop end reaction. Pure acetone is not so readily prepared. I have not been able to secure acetone that assayed more than 99.73 per cent. of pure material, by either Messinger's<sup>3</sup> process or the one presently to be described. This small quantity may have volatilized in course of the work, but the loss would be practically constant for all the methods; consequently, the basis of calculation would be 100, when in reality it is less. Grant that absolutely pure acetone can be made, it is not readily secured when desired.

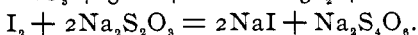
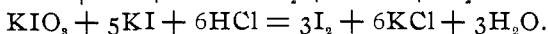
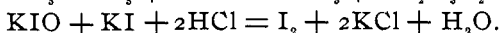
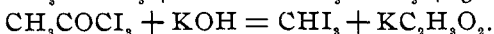
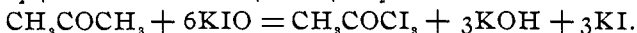
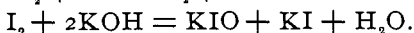
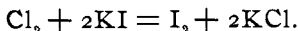
I have modified Dr. Squibb's method so that both the pure

<sup>1</sup> This Journal, 18, 1068; *Ephemeris*, 4, 1759.

<sup>2</sup> 1893: *Mon. Sci.*, (4), 7, Pt. I, 272.

<sup>3</sup> 1888: *Ber. d. chem. Ges.*, 21, 3366.

acetone and the drop end reaction are eliminated. The reactions involved in this process may be represented by the following equations :



There may be some difference of opinion concerning the primary reactions involved, but the basis of calculation is not affected.

The solutions required for this process are as follows :

1. A six per cent. solution of hydrochloric acid.
2. A decinormal solution of sodium thiosulphate.
3. An alkaline potassium iodide solution. To prepare, dissolve 250 grams of pure potassium iodide in distilled water and make up to one liter. Dissolve 257 grams of sodium hydroxide, purified by alcohol, in distilled water and make up to one liter. Allow the insoluble part to subside and mix 800 cc. of the clear solution with the liter of potassium iodide.
4. Sodium hypochlorite solution, about four-fifths normal, or containing from two and six-tenths to three per cent. of available chlorine. To prepare this solution, intimately mix 100 grams of bleaching powder (thirty-five per cent.) with 400 cc. of water. Dissolve 120 grams of crystallized sodium carbonate in 400 cc. of hot distilled water, and immediately pour the latter into the former. Cover the vessel and allow to cool. Then decant the clear liquid, filter the remainder, and to the filtrate add enough water to make up to one liter. To each liter add twenty-five cc. of sodium hydroxide solution, specific gravity 1.29.
5. An aqueous acetone solution containing from one to two per cent. of acetone. This is prepared by weighing the acetone in a beaker containing water, transferring to a graduated cylinder, rinsing the beaker with water and making up to a definite volume.
6. Bicarbonated starch solution. Treat 0.125 grams of starch with five cc. of cold water, then add twenty cc. of boiling water,

and boil a few minutes, cool, and add two grams of sodium bicarbonate.

Having prepared the above solutions, place twenty cc. of the alkaline potassium iodide solution into a suitable flask, add ten cc. of the diluted aqueous acetone; or weigh if greater accuracy is desired; mix well, and run in from a burette, while rotating the flask, an excess of the sodium hypochlorite solution, insert the stopper quickly and shake well for one minute. After agitating, render the mixture acid, by means of the hydrochloric acid solution, add, while rotating the flask, an excess of sodium thiosulphate solution, mix well and allow the mixture to stand a few minutes. Then add the starch indicator and re-titrate the excess of sodium thiosulphate. It is best to add a drop of the sodium hypochlorite in excess and adjust the final reading by means of the sodium thiosulphate.

The relation of the sodium hypochlorite solution to the sodium thiosulphate solution being known, the percentage of acetone can readily be calculated from the above data. One atom of available chlorine will liberate one atom of iodine from the potassium iodide of the alkaline solution, or one cc. will liberate just enough iodine to make one cc. of the same normal strength as the sodium hypochlorite solution originally was; therefore by reading the number of cc. of sodium hypochlorite solution consumed as so many cc. of iodine solution of the same normal strength, we reduce the calculation to the basis of iodine. One molecule of acetone (58) requires three molecules of iodine (759) to form one molecule of iodoform. Expressing it in the form of a proportion, letting  $y$  equal the amount of combined iodine and  $x$  equal the amount of acetone, we have:  $759 : 58 :: y : x$ , or  $x = y \frac{58}{759}$ , or  $x = y \cdot 0.07641$ .

*Example of Calculation.*—Ten cc. of the acetone solution, containing one gram of the solution to be analyzed required 14.57 cc. of  $N \times 0.806$  sodium hypochlorite solution, which formed 14.57 cc. of iodine solution of the same strength; or combining we have  $\frac{14.57 \times 0.806 \times 0.1265 \times 0.07641}{\text{one gram of solution}} = \text{amount of acetone}$   
 $= 11.351$  per cent.

On comparing Messinger's and Dr. Squibb's with the modified

method proposed, using the same solutions, the following results, in per cent. were obtained :

|                                | Messinger. | Squibb. | Kebler. |
|--------------------------------|------------|---------|---------|
| Pure acetone.....              | 99.69      | 99.95   | 99.73   |
| Residue 80° C. and above....   | 20.00      | 19.67   | 20.39   |
| Purified acetone by fraction . | 99.03      | 99.00   | 99.41   |
| Commercial acetone.....        | 96.23      | 96.00   | 96.63   |
| “ “ .....                      | 98.00      | 97.83   | 97.93   |
| “ “ .....                      | 94.30      | 94.00   | 94.46   |
| “ “ .....                      | 94.80      | 94.70   | 94.81   |
| “ “ .....                      | 97.12      | 96.23   | 96.42   |
| “ “ .....                      | 94.93      | 94.80   | 94.39   |
| “ “ .....                      | 96.88      | 96.56   | 96.79   |
| “ “ .....                      | 97.32      | 97.28   | 97.45   |
| “ “ .....                      | 90.74      | 89.03   | 90.51   |
| “ “ .....                      | 98.82      | 96.11   | 98.62   |
| “ “ .....                      | 92.32      | 92.20   | 92.94   |
| Wood alcohol.....              | 14.61      | 14.49   | 14.78   |
| “ “ .....                      | 11.81      | 11.73   | 12.00   |
| Crude wood alcohol.....        | 11.23      | 11.00   | 11.42   |

The above table clearly shows that the results obtained by Dr. Squibb's process are a trifle too low, notwithstanding the fact that its basis of calculation gives it some advantage. The method is represented to give satisfactory results for ordinary work and that it certainly does. The difficulty with the process is in the end reaction. According to some experiments made by me, it is necessary to have present a larger excess of the active agent, to bring about the completed reaction, than the end reaction allows.

The iodoform reaction with ethyl alcohol is an endothermic one, consequently its presence does not interfere with the estimation of acetone, which does not require the presence of external heat to bring about the reaction.

#### LITERATURE ON ESTIMATING ACETONE NOT IN THE BODY OF THE ARTICLE.

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[CONTRIBUTIONS FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 25.]

## DETERMINATION OF POTASH AND PHOSPHORIC ACID IN FODDERS.

CONTRIBUTED BY H. W. WILEY.

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IN the comparative analyses of soils during the past three years we have grown a great number of pot cultures and determined the mineral plant foods in the resulting crops. The following modified potash method, devised by Mr. K. P. McElroy, while not sacrificing accuracy, has made it possible for one analyst to determine the potash, often in duplicate, in more than ten samples a day. Since the quantity of the crop harvested from a poor soil is often small, it is desirable that the phosphoric acid and potash be determined in the same sample.

The method in use for the determination of potash in feeding stuffs, in the laboratory of the United States Department of Agriculture is a simple modification of the ordinary Lindoggladding method, as prescribed by the Association of Official Agricultural Chemists. It is as follows:

Burn eight grams of the substance over a low flame to approximate whiteness. Burning after addition of sulphuric acid does not give more potash than burning alone, and it is more troublesome. Transfer the ash to a 200 cc. flask, using about fifty cc. of water, add five cc. of strong hydrochloric acid and place on the steam-bath for an hour, or boil from five to ten minutes. Add a little iron chloride to precipitate all phosphoric acid as fer-