tate is of variable composition, it should be converted to the dioxide to obtain quantitative results.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF QUEEN'S UNIVERSITY.]

THE ANALYSIS OF ACETONE BY MESSINGER'S METHOD.

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Received September 22, 1919.

In the course of research work extending over the last 6 or 7 years, it was frequently necessary to make accurate determinations of acetone both in large and small amounts. Messinger's method[1] was found to give concordant results under all conditions, and since its accuracy has been disputed by one or two workers, and upheld by others, a résumé of the work on the subject and conclusions are herewith presented.

Since the publication of the original Messinger method, it has been subjected to an extended critical examination by Collischonn,[2] Edward R. Squibb[3] and L. F. Kebler.[4] Perhaps the only fault with all this work lay in the fact that no special precautions were taken to obtain pure acetone, and that the acetone was never weighed out accurately. Since, however, it was desired only to work out the conditions under which concordant results could be obtained, this hardly mattered.

Messinger's method has been seriously criticized only by Vaubel and Scheurer,[5] and by Geelmuyden.[6] The statements of the former authors were conclusively refuted by Keppeler,[7] and those of the latter by Marriott.[8]

Messinger's original results were carried out to an accuracy of only one part in 200. Collischonn[9] made very accurate experiments, but used only a sample of Kahlbaum acetone purified through the bisulfite compound, which distilled within 1°. He carried out other experiments with commercial acetone and showed that concordant results could be obtained.

Squibb and Kebler used sodium hypochlorite solutions, but appear to

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[1] *Ber.*, **29**, 3336 (1888). Other papers on the determination of acetone, not elsewhere referred to, are as follows: G. Kraemer, *Ber.*, **13**, 1000 (1880); E. Hintz, *J. Soc. Chem. Ind.*, **7**, 459 (1888); L. Vignon, *Ibid.*, **9**, 639 (1890); E. Arachesquene, *Ibid.*, **9**, 660 (1890); Otto Folin, *J. Biol. Chem.*, **4**, 177 (1917); T. Stuart Hart, *Ibid.*, **4**, 477 (1918); J. Rakshit, *Analyst*, **41**, 246 (1916).

[2] *Z. anal. Chem.*, **29**, 562–572; *J. Soc. Chem. Ind.*, **10**, 166 (1891).

[3] THIS JOURNAL, **18**, 1068–1079 (1896).

[4] *Ibid.*, **19**, 316–320 (1897).

[5] W. Vaubel and C. Sheuer, *Z. angew. Chem.*, **18**, 215–216 (1905).

[6] H. Chr. Geelmuyden, *J. Chem. Soc.*, **70**, 679 (1896).

[7] G. Keppeler, *Z. angew. Chem.*, **18**, 464–465 (1905).

[8] W. M. Merriott, *J. Biol. Chem.*, **16**, 281 (1913).

[9] *Loc. cit.*

have made up their solutions by putting the weighed acetone directly into water contained in an open beaker and diluting. Their method which is claimed to be an improvement on the original one of Messinger, does not appear to have been adopted elsewhere.

As will be seen from the experiments recorded herewith, Messinger's method gives accurate results if carried out with the precautions specified by Collischonn. The influence of shaking, excess acid, and time of standing seems not, however, to have been fully investigated previously.

Analysis of Acetone by Messinger's Method.

The following procedure, which is practically the standard method recommended everywhere, if strictly adhered to, gives accurate and consistent results.

An amount of acetone in aqueous solution, equivalent to 30–40 mg. is pipetted or added to 50 cc. of *N* sodium hydroxide solution contained in a glass bottle which can be closed with a ground glass stopper. After standing for 5 minutes, about 25% excess of a 0.1 *N* solution of iodine is run in from a buret with continual shaking. It is essential to shake properly or to keep the liquid in continuous rotation. The excess of iodine is needed to complete the reaction.[1] The bottle is then stoppered and the solution allowed to stand for at least 10 minutes (20 minutes in cold weather).

Twenty-five cc. of 2 *N* sulfuric acid is then added from a measuring cylinder, 0.3–0.4 cc. being added in excess of the amount found necessary to neutralize the 50 cc. of caustic soda solution. A 0.05 *N* solution of sodium thiosulfate is then added from a buret until the yellow color just remains visible. Freshly prepared starch solution is now added and the titration finished. 1 cc. of 0.1 *N* iodine = 0.96747 mg. of acetone.

If a larger excess of sulfuric acid is added, too much thiosulfate is required, and the real amount of iodine solution required is thus reduced (see below).

If the bottle is not shaken vigorously while adding the iodine solution, the iodine cannot act completely on the acetone, and as much as 3 times the ordinary amount of thiosulfate may then be required to neutralize the iodine left uncombined, it being transformed into iodate.

The above method of procedure is based on the following experiments:

Method of Preparation of the Acetone Solutions.—750 cc. of British Government acetone was fractionated through a 12-bulb Young stillhead, and the main fraction which distilled at 56.07–56.08° at 761.1 mm. used for analysis.

In preparing acetone solutions it is impossible to pipet out the acetone, or even to weigh it into a beaker containing water as done by Squibb. Loss of acetone cannot be avoided under such conditions. The method

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[1] Collischonn, *Loc. cit.*

employed was to take a calibrated, graduated flask and weigh it while partly filled with water and stoppered. The acetone was delivered into the flask, this shaken and again weighed for the acetone. The flask was then filled to the mark with water and aliquot portions were withdrawn with carefully standardized pipets.

A 36.25% solution of acetone by weight was thus prepared, and of this 5.022 cc. was pipetted out and diluted in another graduated flask to 250 cc.

The thiosulfate and iodine solutions were standardized against each other every 2 or 3 days, and at least once a week against a standard solution of sodium or potassium iodate. Slight changes in strength were, therefore, always allowed for. All pipets, graduated flasks and burets were calibrated several times, and the corrections applied during the work.

The Reproducibility of the Results.

The constancy of results obtained by Messinger's method was first tested. For this purpose 5.022 cc. of the acetone solution prepared as above was pipetted out into glass bottles and analyzed according to the method described. 50 cc. of *N* caustic soda was used, and neutralized for the back titration with 24.4 cc. of sulfuric acid, this being 0.4 cc. in excess. The experimental results obtained were as follows:

TABLE I.

Experiments to Test Concordance.

Expt.	0.1 *N* iodine. Cc.	0.05*N* thiosulfate calculated as 0.1 *N* iodine. Cc.	0.1 *N* iodine used. Cc.
11	40.19	4.08	36.11
12	40.19	4.00	36.19
13	45.20	9.21	35.99
14	45.20	9.29	35.91
16	45.20	8.98	36.22
17	45.20	9.11	36.09
18	45.20	8.95	36.25
19	45.20	9.05	36.15
			Mean, 36.11

It is seen that Messinger's method gives closely concordant results.

On the basis of Expts. 13 and 14, assuming the specific gravity of a 36.25% solution of acetone to be 0.9549, the purity of the acetone would be 97.6%. The iodine solution was 0.09788 *N*. Expts. 16 and 17, give 98.00%; the iodine solution here was 0.09770 *N*.

In common with previous investigators, the difference from 100% was assumed to be water, and a solution thus prepared was used to test Messinger's method further.

Influence of Shaking.—Shaking has a noticeable effect, and experiments were, therefore, run in which the iodine solution was added from a buret to the alkaline acetone solution, without shaking. The stoppered bottle was then shaken occasionally, or sometimes only rarely, so as to vary the conditions as much as possible. The following results were obtained. The iodide acetone solution stood for 20 minutes before being acidified, and in Expts. 7 and 8 for 35 minutes.

TABLE II.

Discordant Results Obtained if Shaking is Omitted.

Expt.	0.1 *N* iodine. Cc.	Thiosulfate equivalent 0.1 *N* iodine. Cc.	Net 0.1 *N* iodine. cc.
2	45.20	11.32	33.88
3	45.20	16.27	28.93
4	45.20	15.69	29.51
5	40.19	11.06	29.13
6	40.19	8.82	31.37
7	40.19	11.80	28.39
8	40.19	13.75	26.44
9	40.19	10.32	29.87
10	40.19	11.00	29.19
15	45.20	16.07	29.13
20	40.19	11.76	28.43

Table II shows that unless the iodine solution is added with continual shaking the results are very discordant.

Influence of Time of Standing.—The effect of time of standing before acidifying with sulfuric acid was next studied. For this purpose a fresh solution of acetone, purified with permanganate and distilled, was made up, containing 4.185 g. in 100 cc. of which 25.026 cc. was diluted to 250 cc. and 5.022 cc. pipetted out for analysis. The following results were obtained:

TABLE III.

Influence of Time of Standing Before Acidifying.

Expt.	0.1 *N* iodine. Cc.	Thiosulfate equivalent 0.1 *N* iodine. Cc.	Net 0.1 *N* iodine used. Cc.	Time of standing. Min.
53	35.17	12.94	22.23	20
54	35.17	12.91	22.26	20
55	35.17	12.88	22.29	20
51	35.17	12.94	22.23	5
52	35.17	12.87	22.30	5
56	35.17	12.87	22.30	5
57	35.17	12.93	22.24	5

Mean, 22.26

Five minutes standing is, therefore, sufficient, as has already been pointed out by previous experimenters, although 20 minutes does no harm. My practice is to let solutions stand for 20 minutes, since in cold weather the reaction takes a longer time for completion.

Another point in this connection required elucidation. For some reason previous experimenters, in their directions for making the analysis, have specified that after adding the acetone to the caustic soda solution, the solution should stand for 5 min. I had supposed that there might be some reason for this, since alkalies effect a change to di-acetone,[1] but experiments were finally made to clear up this point. In one analysis run as usual, the net iodine used was 22.93 cc. A similar experiment in which the iodine solution was added to the acetone caustic soda solution directly after mixing gave the net amount of iodine used as 22.93 cc. It would, therefore, appear to be unnecessary to wait for 5 minutes before adding the iodine solution.

Effect of Varying Amounts of Acid on the Titration.—When excess of acid is used a larger amount of thiosulfate solution is required for the back titration. The following experiments make this point clear:

Blank experiments were run by adding a known amount of iodine solution to the caustic soda, letting stand for 20 minutes, acidifying and titrating back. The 50 cc. of N caustic soda used required 23.9 cc. of sulfuric acid for neutralization.

TABLE IV.

Effect of Varying Amounts of Sulfuric Acid.

Expt.	0.1 N iodine taken. Cc.	2 N sulfuric acid. Cc.	0.1 N iodine used. Cc.	Excess thiosulfate as 0.1 N iodine. Cc.
3A	7.07	26.0	7.24	+0.17
4A	7.07	27.0	7.28	+0.21
5A	7.07	25.0	7.17	+0.10
6A	7.07	25.5	7.22	+0.15
7A	7.07	24.0	7.11	+0.04
8A	8.08	24.1	8.08	0.00
9A	10.10	25.0	10.10	0.00

To get accurate results it is, therefore, advizable to use about 0.5 cc. excess of 2 N sulfuric acid.

Expts. 8A and 9A show that there was no nitrite or alcohol in the caustic soda used.

TABLE V.

Effect of Using a Stoppered Bottle or an Open Flask.

Expt.	Conditions.	0.1 N iodine. Cc.	Thiosulfate equivalent to 0.1 N iodine. Cc.	Net 0.1 N iodine used. Cc.
7B	Stoppered bottle	28.48	7.40	21.12
8B	Stoppered bottle	28.62	7.52	21.14
9B	Stoppered bottle	28.17	7.17	21.14
10B	Stoppered bottle	35.30	14.17	21.13
			Mean,	21.13
11B	Open flask	29.59	8.90	20.74
12B	Open flask	30.17	9.64	20.56
13B	Open flask	28.46	7.80	20.70
			Mean,	20.67

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[1] A. Hoffman, THIS JOURNAL, 31, 723 (1909).

In experiments undertaken some 6 years ago when acetone determinations of not as high a degree of accuracy had to be made, the titrations were carried out in an open bottle. It seemed of interest to determine the error thus introduced. The preceding results were obtained.

The results show that less iodine is required when an open flask is used. This was confirmed by another series of experiments run in the same manner in which the mean of 5 determinations in an open flask was 20.43 cc. iodine, as against a mean of 20.71 cc. for 3 experiments carried out in a stoppered bottle.

The Influence of Dilution.—W. M. Marriott[1] has recently published experiments showing that accurate results can be obtained even at great dilution. My own experiments lead to the same conclusion, and I, therefore, refrain from quoting any further evidence on this point.

The Influence of Methyl and Ethyl Alcohol.—Previous investigators had aways assumed that methyl alcohol was without influence on the titration, although they recognized that ethyl alcohol had some influence.

Rakshit[2] worked out a method for estimating acetone in presence of ethyl alcohol, and found that this could be done with accuracy if lime water or barium hydroxide was used instead of caustic soda in the Messinger method. He makes a correction of 0.8 cc. of 0.2 *N* iodine solution for each one cc. of ethyl alcohol present. He states that the method can be used with as many as 10 parts of ethyl alcohol to one part of acetone. He found also that one cc. of methyl alcohol has no effect on his method. Kebler[3] found that one cc. of ethyl alcohol required a correction of 0.8 cc. of 0.1 *N* iodine. The experiments listed below show that a certain error is introduced by the presence of methyl alcohol. Experiments were run as usual, but with the addition of 0.5 cc. of pure methyl alcohol. Expt. 97 was a blank. The methyl alcohol used in Expt. 98 had been dried with lime and redistilled.

TABLE VI.

Influence of Methyl Alcohol.

Expt.	0.1 *N* iodine. Cc.	Thiosulfate equivalent 0.1 *N* iodine. Cc.	Net 0.1 *N* iodine used. Cc.
97	10.10	0.04	0.06
91	10.10	9.78	0.32
92	10.10	8.36	1.74
93	10.10	9.69	0.41
94	10.10	9.50	0.60
97	10.30	9.74	0.56
98	10.30	9.84	0.46

It may be concluded that 0.5 cc. of methyl alcohol causes an error of nearly 0.5 cc. in the amount of 0.1 *N* iodine solution used.

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[1] *Loc. cit.*

[2] Jitendranath Rakshit, *Analyst*, 41, 246 (1916).

[3] Kebler, *Loc. cit.*

When the present paper was nearly completed, a short note by A. J. Field[1] was found. He states that Collischonn's method is unsatisfactory, but quotes no experimental evidence, and his failure to obtain concordant results is probably due to non-observance of the precautions to be adopted, and more possibly due to adding varying amounts of acid for the back titration. He states, however, that "if after the addition of the iodine solution, the mixture is shaken for 5 minutes, a low result is obtained, while shaking for 20 minutes gives a higher result, the percentage varying with the length of time of agitation." This is quite contrary to the experiments recorded above, but two additional experiments were nevertheless run to test the point. An acetone solution was titrated, the iodine solution being added to the acetone caustic soda solution, without shaking, and the stoppered bottle was then shaken vigorously while standing, for 5 minutes, and for 20 minutes, respectively. The net amounts of iodine used were identical—22.26 and 22.26 cc. The theoretical amount of iodine used when carrying out the titration under the conditions specified in this paper, that is, running in the iodine solution with continual agitation, was 22.26 cc.

Summary.

(1) It has been shown that Messinger's method for the analysis of acetone gives accurate and concordant results under proper conditions.

(2) The influence of standing, method of adding the iodine solution and shaking, effects of excess acid, and dilution have been studied and found not to influence the results under proper conditions.

(3) Methyl alcohol and ethyl alcohol both use up a certain amount of iodine solution.

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[CONTRIBUTION FROM THE MINNESOTA AGRICULTURAL EXPERIMENT STATION.]

A SIMPLE HYDROGEN ELECTRODE.[2]

BY C. H. BAILEY.

Received September 25, 1919.

The considerable number of hydrogen electrodes that have been described in the literature suggests either that these devices have not been wholly perfected, or that electrodes suited to one purpose may not be adapted to other uses. Moreover, several of the forms that have been proposed are expensive; most of them are somewhat complicated and fragile and their construction presents an impossible undertaking for the average amateur glass blower.

This laboratory has had occasion to make a large number of hydrogen-

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[1] *J. Ind. Eng. Chem.*, 10, 552 (1918).

[2] Published with the approval of the Director as Paper No. 180, of the Journal Series of the Minnesota Agricultural Experiment Station.