

## VOLUMETRIC DETERMINATION OF ACETONE.<sup>1</sup>

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Received November 9, 1896.

IN the *Moniteur Scientifique* of 1893, 41, 4 Serie, Vol. 7, 1<sup>o</sup>, p. 272-274, MM. J. Robiueau and G. Rollin publish a paper entitled, "Dosage Volumetrique de L'Acetone," and the following is, first, a free translation and abridgement of this paper; and second, the detail of an improvement of the process whereby it is rendered easier, more simple, quicker, and better adapted to technical uses, whilst still sufficiently accurate for most purposes.

### FIRST, FREE TRANSLATION.

The common way of determining the proportion of acetone in a liquid containing it is to convert the acetone into iodoform by means of iodine in the presence of soda after eliminating from the liquid everything that would interfere with the proper reaction.

For this process binormal solutions of iodine and of sodium hydroxide are used, and the precipitated iodoform is washed, dried, and weighed, or is dissolved in ether, and the whole or a fraction of the ethereal solution is dried over sulphuric acid and weighed.

The appreciable volatility of iodoform at ordinary temperatures introduces a source of error that is objectionable, especially when dealing with small quantities.

But, aside from this, the time required for this process is relatively so long that we have sought to change it to a volumetric process that is more rapid.

Our proceeding consists in mixing the acetone with a solution of potassium iodide and sodium hydroxide, and then transforming it into iodoform with a titrated solution of a hypochlorite. The end reaction is indicated by the appearance of a blue color, when a drop of the liquid is touched with a drop of bicarbonated starch solution.

From the quantity of hypochlorite used the quantity of acetone is deduced.

<sup>1</sup> Read before the New York Section of the American Chemical Society, November 6th, 1896.

For it happens that the presence of even the smallest trace of an alkaline hypiodite, in a solution of soda, gives a blue color with a starch solution which contains an excess of sodium bicarbonate.

Again, a liquid containing acetone, an iodide and caustic soda in excess, and into which a solution of hypochlorite is passed, gives no reaction with bicarbonated starch until the whole of the acetone is converted into iodoform.

This proceeding, however, only gives constant results when certain precautions are taken. Unless the liquid containing the acetone be sufficiently alkaline, an excess of hypochlorite will be required to decompose all the acetone.

The potassium iodide must be in excess.

The dilution must be fairly uniform, and the concentration of the hypochlorite about the same for the different titrations.

The process should not be used in too strong a light.

It is very important that the liquid should be constantly stirred during the additions of the hypochlorite.

The strength of the hypochlorite solution is ascertained by trial against a pure acetone made by the bisulphite process.

#### PREPARATION OF THE HYPOCHLORITE.

For the titration of liquids containing considerable proportions of acetone, the hypochlorite solution is prepared as follows :

To 500 cc. of the concentrated solution of sodium hypochlorite of commerce, which tests from forty-five to fifty-five volumes of chlorine, an equal measure of water, and ten cc. of solution of pure soda of 36° B., are added, and the solution is kept in an amber colored bottle, well corked.

#### TITRATION OF THE HYPOCHLORITE SOLUTION.

About two grams of pure acetone from bisulphite is weighed off and diluted to 500 cc.

Then ten grams of pure potassium iodide is put into a conical Bohemian beaker and 100 cc. of the diluted acetone and twenty cc. of solution of caustic soda of 28° B. are successively added, and the whole is stirred until the iodide is dissolved and the liquid is homogeneous.

Into this the hypochlorite solution is passed drop by drop from a burette, with constant stirring, precipitating the iodoform in large flakes which easily settle out. When farther additions of the hypochlorite give but a light cloudiness a drop of the liquid is transferred to a white porcelain plate by means of a glass rod and is there brought in contact with a drop of the bicarbonated starch solution. As soon as the hypochlorite is in excess the blue color appears very distinctly. The volume of hypochlorite used is then read off from the burette, and then for security of result the titration is repeated.

*Example.*—2.081 grams pure acetone is weighed off and diluted to 500 cc; 100 cc. of this solution requires 22.5 cc. of the hypochlorite. This gives for each cc. of hypochlorite 0.01874 gram of pure acetone. These results are liable to vary a little if the conditions of the experiment vary much. The stirring is supposed to be constant, and the hypochlorite solution to be regularly added.

If to 100 cc. of the diluted acetone 100 cc. of water be added and the same quantities of iodide and soda as above, 22.05 cc. of hypochlorite is required instead of 22.5 cc. In using forty cc. of the soda solution instead of twenty cc., twenty-two cc. of the hypochlorite is required. In using sixty cc. of soda solution instead of twenty cc., 21.6 cc. of the hypochlorite is required. In using ten cc. of soda instead of twenty cc., twenty-three cc. of the hypochlorite is required.

These results show that dilution of the acetone and a small excess of soda have but little influence, but that a deficiency in alkalinity has a very considerable effect on the quantity of hypochlorite required. And farther, that the alkalinity indicated by twenty cc. of soda solution of 28° B. appears to be normal.

Under the given conditions of alkalinity and dilution the relations between acetone and the available chlorine of the hypochlorite is obviously one molecule of acetone to six atoms of chlorine.

The solution of hypochlorite used by us was the liquor of Penot, testing 21.56 volumes.

The titration of the hypochlorite with pure acetone may be

omitted, simply determining the available chlorine of the liquor of Penot instead, but we prefer the titration with pure acetone.

#### DETERMINATION OF ACETONE IN A COMPLEX LIQUID.

We give as an example of this the titration of a complex liquid made with precision, which liquid has served us to control the accuracy of the process.

The complex liquid contained :

1.510	grams water,	} 39.98 per cent. acetone.
1.677	“ ethyl alcohol,	
1.550	“ methyl alcohol, pure	
3.149	“ acetone, pure from bisulphite	

Of this mixture 3.2445 grams was weighed off and diluted to 500 cc. Proceeding as before 100 cc. of this dilution, ten grams of potassium iodide, and twenty cc. of soda solution of 28° B. required 13.85 cc. of the hypochlorite. This by calculation gives 39.99 per cent. of acetone, and thus verifies the composition of the complex liquid; and it is seen that the presence of ethyl alcohol is without influence on the result.

The effect of the presence of paraldehyde in the same complex liquid was tried by a similar titration.

To 100 cc. of the complex solution corresponding to 0.4162 gram of pure acetone, ten cc. of an aqueous solution containing five per cent. of pure paraldehyde was added (say one-half gram) or a little more paraldehyde than acetone. This mixture took 22.4 cc. of the hypochlorite instead of 22.2 cc. as required.

This variation is slight for the relatively large proportion of paraldehyde, and is greater for larger proportions, but instances are rare in which paraldehyde is present in such proportions.

In all such instances where the presence of the aldehyde has been established by the process of Bardy, the acetone should be purified by this process before titration.

For the determination of acetone in very dilute solutions a solution of hypochlorite of one-fifth of the above strength is preferred. That is, a solution containing four or five volumes of available chlorine, and the degree of alkalinity should be proportionately reduced.

With a little practice it is easy to judge as to how much acetone is present in a liquid to be titrated, and from this to judge

of the corresponding quantity of hypochlorite required, and in this way keep the conditions of the method nearly uniform, and the more uniform the conditions the more constant the results.

This process has the great advantage of being rapid, and thus of permitting a number of titrations being made in a short time with results sufficiently accurate.

#### REMARKS.

The reaction used in this titration is very delicate, and where traces of acetone are concerned it is better seen when there is excess of iodide and of soda and but little hypochlorite. An aqueous solution of 0.004 gram of acetone in the liter gives a heavy cloudiness immediately. The reaction with 0.0012 gram of acetone in the liter is seen in a few moments. With 0.0008 gram to the liter the reaction is difficult to see. This reaction should not be made in a bright light. In sunshine or in a very bright light the traces of iodoform produced disappear very rapidly, the liquid becoming clear, but in a dim light the precipitate does not disappear.

The titrated solution of hypochlorite should be kept in amber-colored glass in a cool place and sheltered from bright light. The titration should be frequently repeated, because it varies rather rapidly, especially when diluted. We have made a series of experiments on this point, which strikingly show these variations under different influences. A solution of hypochlorite prepared for titrations gave 22.16 volumes of available chlorine; kept in a cool place, in obscurity for six days, it gave 21.96; kept in colorless glass, corked, in a bright light, most of the time in sunlight, for seven days, it gave 12.32. In a water-bath at 100° C. for a quarter of an hour it gave, when cooled, 19.48.

#### END OF TRANSLATION.

The rapidly increasing uses of acetone in the three years that have passed since the publication of this important paper of Robineau and Rollin have given to it so much additional importance that it seemed well to the present writer—who early adopted this volumetric method—to attempt to modify the method in the direction of greater simplicity and rapidity, even

if this should be at the cost of a little of its accuracy. As acetone comes more and more to take the place of both ethyl and methyl alcohol as much the better solvent for most purposes, and as its manufacture is cheapened, it becomes more and more desirable to have a rapid and easy way of estimating its proportions in mixtures or under conditions to which specific gravity is not applicable.

Therefore, taking the above quoted paper as a basis, and giving full credit to the authors of it for every important principle and step of the method, the following slight modifications are offered as the result of about three months' experience with the original process and over a year's experience with the modifications.

#### STANDARD SOLUTION OF ACETONE.

A flask of 100 cc. capacity containing about fifty cc. of distilled water is carefully weighed. To this is added about thirteen cc. of pure acetone, made by the bisulphite process. The weight is then again taken, when it will be found that the acetone added is a fraction more or less than ten grams. The dilution is then transferred to a measuring flask, the weighing flask being rinsed in and is farther diluted with distilled water until each ten cc. of the dilution contains one-tenth gram of acetone. This is kept in a well stoppered bottle of dark glass, for, although the writer has no evidence of any change taking place in acetone, and believes it to be quite as permanent as ethyl alcohol, still it may be well to keep a dilute standard solution protected against bright light.

Of this solution or dilution ten cc. equal to one-tenth gram of acetone, is accurately measured off for each titration of the solution of hypochlorite.

#### SOLUTION OF POTASSIUM IODIDE.

Of this salt 250 grams are dissolved in distilled water, and the solution is made up to one liter, when each ten cc. will contain two and a half grams of the iodide.

#### SOLUTION OF SODIUM HYDROXIDE.

Of commercial caustic soda, purified by alcohol, 257 grams is dissolved in distilled water, the solution made up to one liter,

and set aside until it settles quite clear. Then 850 cc. of clear solution is poured off and added to the solution of potassium iodide, making 1,850 cc. of total solution.

Of this solution twenty cc. is taken for each titration.

The remainder of the soda solution is again allowed to settle clear for farther use in the hypochlorite solution.

#### SOLUTION OF SODIUM HYPOCHLORITE.

The officinal solution of chlorinated soda of the U. S. Pharmacopœia ("Liquor Sodæ Chloratæ," U. S. P.) answers very well for this process, the officinal strength of two and six-tenths per cent. of available chlorine being quite convenient.

To a liter of this solution in a bottle of dark glass, twenty-five cc. of the above described clear soda solution is added and the mixture well shaken.

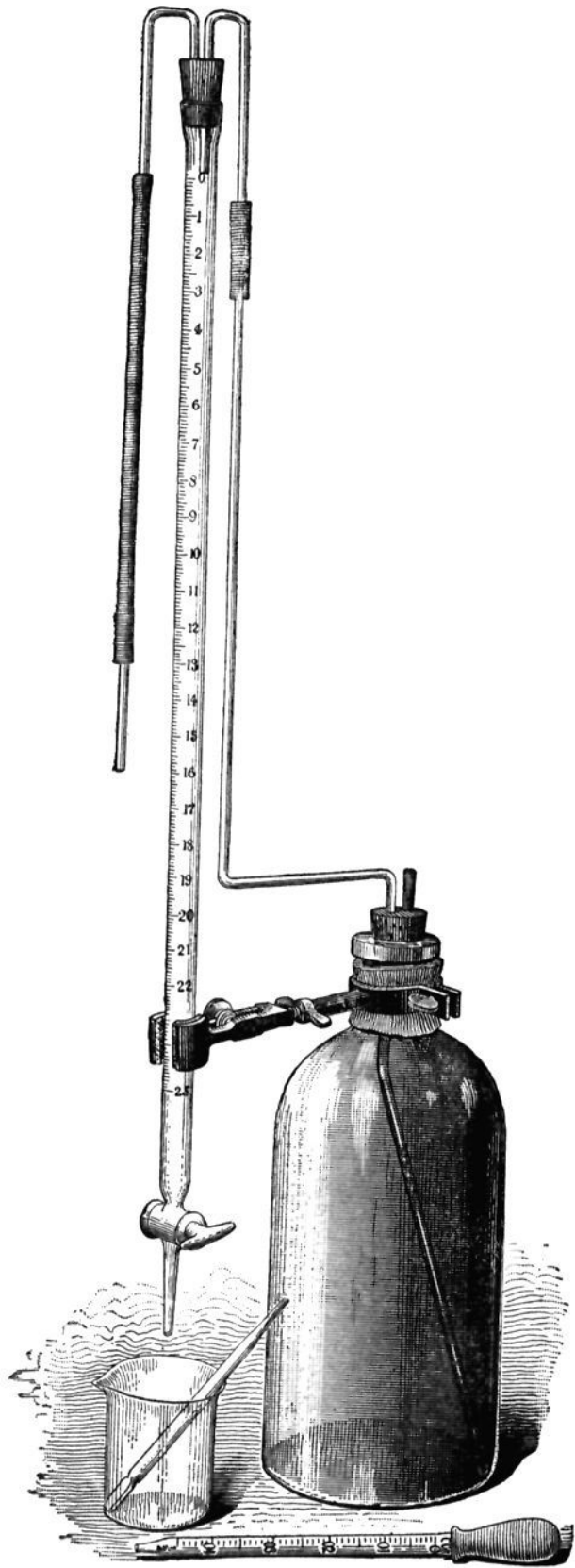
If in buying the "Solution of Chlorinated Soda" of the U. S. P. for this process it should be found, as is not unfrequently the case, weaker than is required by the U. S. P., or, if by keeping it becomes weaker, this will be at once discovered on balancing it against the standard acetone solution, and so long as the one-tenth gram of acetone does not require more than say twenty cc. of the more dilute hypochlorite, the formula need not be modified.

If there be much of this titration to do it is very convenient to fit this bottle with an automatic zero burette,<sup>1</sup> as shown in the following illustration, this form being, so far as is known, original with the writer and very convenient for general rapid working with a burette. The advantage is, beside that of rapid and easy working, that it does not require a special burette and is easily fitted up from the resources of any laboratory.

#### BICARBONATED STARCH SOLUTION.

Starch, 0.125 gram, is mixed with five cc. of cold water, and then added to twenty cc. of boiling water and boiled. When cold two grams of sodium acid carbonate is added and stirred until dissolved. Kept in a colorless bottle this solution does not sensibly diminish in delicacy or reaction in three months. But for how much longer it would remain good for this reaction was not tried.

<sup>1</sup> This Journal, 16, 143.



AUTOMATIC ZERO BURETTE.



## THE TITRATION.

The burette being filled with the solution of sodium hypochlorite, ten cc. of the standard solution of acetone (equal to one-tenth gram of acetone) is measured into a beaker of about fifty cc. capacity, and twenty cc. of the mixed solution of iodide and soda is added and stirred well. Into this the hypochlorite solution is passed in rapid dropping, with constant stirring, until eight or ten cc. has been run in. Then the precipitated iodoform is allowed to settle out, and a drop or two more hypochlorite is added. Should this produce a dense cloudiness one-half cc. more hypochlorite is added, and well stirred and again allowed to settle. Then a drop or two more of hypochlorite is added. If there should still be a cloudiness, another one-half cc. of the hypochlorite is added and well stirred, and so on until the cloudiness is very slight. Then the starch testing begins.

A small drop of the liquid is transferred by a rod to a white porcelain tile or plate, and a similar small drop of the starch solution is placed very near it. Then with the first rod the drops are made to connect by a fine line, so that the whole has a dumb-bell form. If there be no blue color, one or two-tenths cc. more of the hypochlorite is added and well stirred, and the testing is repeated, until finally a blue line will be seen at the moment of contact of one drop with the other. If the last negative testing has taken 10.4 cc. from the burette, and this positive testing, which has given the blue line, required 10.6 cc., then the accepted reading would be 10.5 cc., and this would be the hypochlorite equivalent of one-tenth gram of acetone. If the blue line be very faint, it will be momentary only, and will indicate that the excess of hypochlorite is very small, and that 10.6 cc. is a closer reading than 10.5, but the process is not sufficiently accurate to take much account of such differences, since even with much experience and great care it is hardly practicable to get any two titrations to agree within one-tenth cc. of hypochlorite.

Having then 10.5 cc. as the hypochlorite equivalent of one-tenth gram of acetone at this time, it is easy to estimate any smaller or larger quantity of acetone that requires a smaller or

larger quantity of the hypochlorite by the equation  $10.5 : 0.1 :: a : x$ .

But this hypochlorite solution is liable to diminish in strength by keeping, and therefore must be standardized by this standard acetone solution as often as the accuracy of the determinations may require. At times the change in strength is scarcely perceptible from day to day in several successive day's work, but in standing for a week or two there will always be a falling off in strength to the extent of one-tenth to five-tenths cc. in the hypochlorite. The addition of the soda solution appears to render the hypochlorite more permanent, just as the sodium bicarbonate renders the starch solution more permanent. But in the case of the starch the blue reaction does not occur if the bicarbonate be not present.

The titration of the acetone present in unknown dilutions requires first that the strength should be estimated by known conditions or by sensible properties, in order to keep the proportions of the reagents and the dilutions approximately the same, or at least not differing very widely when close determinations are required. If then the taste and smell should indicate that the acetone to be tested is below twenty-five per cent., four-tenths cc. may be taken for the testing. If over twenty-five per cent. and under fifty per cent., two-tenths cc. may be taken. If over fifty per cent., one-tenth cc. is sufficient.

For the adjustment of these small quantities with a sufficient degree of accuracy for rapid technical working, it is convenient to have a five-tenths cc. pipette divided in 0.01 cc. fitted with a rubber bulb, as shown in the illustration. By screwing the neck of this bulb up or down upon the glass, with the point in the liquid, close measurements may be quickly made.

A beaker of fifty cc. capacity containing ten cc. of water is weighed and the weight noted. The four-tenths, two-tenths, or one-tenth cc. of the sample to be titrated is delivered in the water and the weight again taken to give the quantity of the sample taken for the titration. Then the twenty cc. of the iodide and soda solution is added, the whole well stirred, and the hypochlorite dropped in, and the end reaction managed precisely as described in standardizing the hypochlorite, and the quantity of

hypochlorite used is noted. Then as 10.5 cc. of the hypochlorite is to one-tenth gram of acetone, so is the quantity of hypochlorite now used to the quantity of acetone present in the portion of the sample taken for titration. Then as the weight of this portion taken for titration is to the quantity of acetone found in it, so is 100 to the percentage of acetone in the sample.

For example, a sample supposed to be not far from absolute is to be titrated. A fifty cc. beaker with ten cc. of water weighs 25.283 grams; with one-tenth cc. of the sample added the weight becomes 25.360 grams, giving 0.077 gram as the weight taken for the titration. To this is added the twenty cc. of iodide and soda solution, and the mixture being well stirred, the hypochlorite is dropped into saturation when seven and nine-tenths cc. is found to have been used. Then as 10.5 is to one-tenth, so is seven and nine-tenths to 0.0752 gram of acetone in the 0.077 gram of the sample taken. Then as 0.077 gram of the sample taken is to the 0.0752 of acetone indicated, so is 100 to 97.66 per cent. of acetone in the sample.

This is the rationale of the operation, but the calculation is shortened by simply dividing the standard hypochlorite (10.5 cc.) into the hypochlorite required (seven and nine-tenths cc.) to get the corresponding acetone (0.0752 gram), and then dividing the weight of the sample taken (0.077 gram) into the weight of acetone obtained from it (0.0752 gram) to get the percentage proportion of the acetone (97.66 per cent.).

Of course the method of definite dilution, and the titration of an aliquot part, as described in the original paper of Robineau and Rollin (see translation) is available and more accurate than that here recommended, and takes but little more time.

Where acetone is made, or is much used, and especially in processes where it is recovered by distillation to be used over again, there is often much need of testing the strength of very weak dilutions, and of knowing when acetone is absent. In many such uses accuracy is not required and rough estimates are sufficient. For work of this kind, especially when the strength is below ten per cent., the weighing of the sample to be tested may be omitted, because the specific gravity is so nearly

that of water that the measure may be accepted as cubic centimeter for gram.

DETERMINATION OF ACETONE IN THE PRESENCE OF ETHYL ALCOHOL.

The standard dilution of acetone containing ten grams in the liter was used, and ten cc. of this required 14.3 cc. of the hypochlorite solution. On repetition 14.4 cc. was required.

A dilution of ethyl alcohol was made containing ten grams in the liter, and ten cc. of this requires one-tenth cc. of the hypochlorite. On repetition 0.125 cc. was required.

To ten cc. of the acetone dilution two-tenths cc. of the alcohol dilution was added, and this mixture required 14.4 cc. of the hypochlorite solution. On repetition 14.4 cc. again was required.

To ten cc. of the alcohol dilution two-tenths cc. of the acetone dilution was added, and this mixture required 0.35 cc. of the hypochlorite. On repetition four-tenths cc. was required.

In each case ten cc. of the iodine and soda solution was used and all other conditions were kept fairly uniform.

In the case wherein the hypochlorite was added to alcohol alone no precipitate nor cloudiness was visible, although 0.1 to 0.125 cc. was required to obtain the starch reaction. When acetone had been added to the alcohol one-half this quantity of the hypochlorite was sufficient to give decided cloudiness.

These results appear to confirm the conclusions of Robineau and Rollin to the effect that the presence of ethyl alcohol has no effect upon the titration of acetone by this method, although ethyl alcohol is an iodoform-yielding substance. The small quantity of hypochlorite required to obtain the starch reaction when alcohol alone was titrated was probably in consequence of traces of impurity in the alcohol.

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THE DETERMINATION OF SULPHUR IN CAST IRON.

BY FRANCIS C. PHILLIPS.  
Received November 10, 1896.

IN a paper read before the American Chemical Society in August, 1895,<sup>1</sup> I have detailed some experiments made in the determination of sulphur in white cast iron by the evolution method, and have attempted to show that the loss of sulphur in its

<sup>1</sup> This Journal, 17, 891.