A METHOD FOR THE DETERMINATION OF
SMALL AMOUNTS OF CHLORINE

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*Approved
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A METHOD FOR THE DETERMINATION OF
SMALL AMOUNTS OF CHLORINE

In spite of the large amount of work that has been done on the determination of chlorine there are at present only three methods in general use, the gravimetric one of precipitating the chlorine as silver chloride and the volumetric methods of Volhard and Mohr. For extremely small amounts of chlorine, as for example, chlorine occluded in barium sulphate precipitated in the presence of barium chloride there has been no method. The only method applicable for acid solutions, the Volhard, calls for solution in nitric acid, in which barium sulphate is insoluble. The proposed method is for the determination of those very small amounts and is applicable to all substances soluble in hot concentrated sulphuric acid and also in mixtures of sulphuric and nitric acids.

Of the present methods, the Mohr is applicable only to a neutral or very slightly alkaline solution. It consists in titrating the chlorides with a standard solution of silver nitrate using potassium chromate as an indicator. After all the chloride is precipitated by the silver nitrate the next drop of the silver nitrate

produces a red precipitate of silver chromate. For small amounts of chlorides in a concentrated solution, the method is very accurate. This method is very extensively used in water analysis as it is quick and accurate. Outside of this, however, it is but seldom used.

Volhard's method is the one that is almost universally used, from the fact that it is applicable to the titration of chlorine in acid solution. When solutions of silver and an alkali thiocyanate are mixed in the presence of a ferric salt, the thiocyanate combines with the silver to form insoluble white silver thiocyanate. The next drop of excess thiocyanate then forms the red ferric thiocyanate. A saturated solution of ferric ammonium alum to which has been added sufficient nitric acid to remove the red color is used for the indicator. An excess of silver nitrate is added to the nitric acid solution of the chloride, the AgCl is then filtered off and the excess silver nitrate is titrated with either ammonium or potassium thiocyanate, generally the former, using 5 c.c. of a saturated solution of ferric ammonium alum, as indicator. Volhard's original directions did not provide for the filtration of the AgCl but it was found by G. Drechsel (1) and later confirmed by M. A. Rosanoff and A. E. Hill (2) that the silver chloride reacted with

the red ferric thiocyanate making the end point uncertain and the results low. We will refer to this later in the discussion. Neither of these methods provide for extremely small amounts of chlorine as occluded chlorine in precipitates insoluble in nitric acid.

The first suggestion for this work was found in a paper on "Chlorine in Barium Sulphate Precipitated in the Presence of Barium Chloride" by G. A. Hulett and L. H. Duschak. (3) In this paper, the authors, in determining the amount of occluded barium chloride in barium sulphate precipitated in the usual manner made use of the foregoing method. The following is that part of the article that deals with the method in question.

"Chlorine in Barium Sulphate Precipitated
in the Presence of Barium Chloride."

G. A. Hulett and L. H. Duschak.

"Barium sulphate is easily soluble in concentrated sulphuric acid. From the sulphuric acid solution the chlorine is easily and completely driven off as HCl by means of an inert gas. The HCl can be determined in an excess of N/100 silver nitrate solution, a definite amount of which is poured into two washing

flasks. The chlorine determination is done in the flask in which the excess silver nitrate is titrated. We find that a stream of purified air drives the entire amount of HCl from the sulphuric acid solution within two hours. At no time have we found HCl in the second flask. The chlorine can be determined in this manner to the 1/100 part of a milligram. The method also gives very trustworthy results which follow from the following experiments. Moreover the actual time necessary for the analysis is short.

"To prove the method, a well mixed sample of barium chloride was introduced in a little tube and concentrated chlorine free sulphuric acid added. The second tube contained standardized silver nitrate solution. The other end of the tube containing sulphuric acid was warmed with water and a stream of purified air conducted through the system of tubes. Within two hours after the salt is dissolved, the HCl is completely gone from the sulphuric acid solution.

"In the following analysis, the one is the amount of barium chloride weighed out by us and the other is determined by the chlorine determination. The silver chloride in the last two experiments was determined gravimetrically in a Gooch crucible.

"These are the first analyses made according to this method. According to the several experiments which we have made in the meantime the method gives results accurate to .01 milligrams."

<u>BaCl₂·2H₂O</u> <u>weighed</u>	<u>BaCl₂·2H₂O</u> <u>found</u>	<u>error.</u>
14.65 mg.	14.64 mg.	- .01 mg.
14.02	14.09	/ .07
12.66	12.59	- .07
7.23	7.28	/ .05
14.30	14.30 (grav.)	.00
22.40	22.39 (grav.)	- .01

The method has never been confirmed although it has been used since. Allen and Johnson (4) in a paper on "The ~~Exact~~ Estimation of Sulphates in Soluble Sulphates" makes use of the method.

In support of the method the authors offer only six determinations on the basis of which they claim that it is accurate to .01 mg. Of the six results, four are volumetric determinations and show errors of -.01, / .07, -.07, / .05 mg. The gravimetric determinations show errors of .00 and -.01 mg. An insufficient number of determinations

have been given and the six offered do not bear out the accuracy claimed. It is therefore the purpose of this paper to investigate the method and determine the accuracy obtainable. To do this the plan adopted was that of weighing out definite amounts of several chlorides and determining the chlorine content by the proposed method.

The following page gives a drawing of the apparatus used. The air is first passed through a 15% solution of silver nitrate to insure its freedom from chlorides. (C) is the digestion chamber containing concentrated sulphuric acid. The tube (b) is a capillary the purpose of which is to break up the bubbles of air as small as possible. The delivery tube is run deep into a long narrow test-tube, containing the N/100 silver nitrate. The digestion chamber is set in a water bath which is kept at 99°C. A ground glass stopper (d) is provided through which the substance is introduced.

One detail of manipulation was used, the suggestion of Prof. J. A. Gibson, which could be used with advantage in other work. This is the use of gelatine capsules. The substance is weighed out into #00 capsules which are then very easily introduced into the apparatus. When left in a balance case over night

even in a damp atmosphere they are non-hydrosopic. They should be exposed for a time in the same atmosphere as the balance as they are slightly hydrosopic when brought from a dry to a damp place. Two blanks run on these capsules showed no trace of chlorine. One blank on 40 capsules, ten from four different packages of 100 each, showed no trace of chlorine. The other blank on 20 from one package of 100 showed no chlorine.

The digestion chamber contained 15 c.c. of chlorine free concentrated sulphuric acid. The capsule is first introduced through (d), the stopper then closed and the air turned on. A very slow stream of air is conducted through the apparatus. After the air starts the test-tube (f) is then put in place. By this means any error due to wetting the inside of the discharge tube with silver nitrate which might not be all converted into silver chloride is avoided. Three or four minutes are necessary for the sulphuric acid to break up the gelatine capsule. The substance is then dissolved in the sulphuric acid and the chlorine evolved as HCl which is then absorbed by the silver nitrate. The air current is passed through the system for two hours, after which the AgCl is filtered on a 7 cm. filter paper, washed free from silver nitrate

with water containing a very little nitric acid, 10 c.c. 1:1 nitric acid and 5 c.c. ferric alum solution added, and the solution then titrated with N/100 ammonium thiocyanate.

The endpoint of this reaction is somewhat indistinct due to the dilution of the solutions. However the solution is first cooled in ice and then titrated to a definite color. The ammonium thiocyanate is then run against the silver nitrate to the same depth of color. The silver nitrate is standardized in triplicate by precipitating 50 c.c. of the silver nitrate with HCl and weighing the precipitated AgCl on a Gooch crucible. In all of the work, weight burettes were used for the silver nitrate and the ammonium sulphocyanate as an accuracy to .01 g. by weight is easily attained and the accuracy by volume to .02 c.c. is questionable. An assay balance reading to .00001 g. was used for weighing the salt.

The substances used for examination were barium chloride, sodium chloride and lead chloride. Merck's barium chloride was used. The sodium chloride was made by passing purified chlorine into a concentrated solution

of sodium chloride, filtering and fusing the precipitate. The lead chloride was made by recrystallizing lead nitrate, precipitating with HCl and drying at 140° C. The purity of all of the salts was checked by dissolving a weighed amount in nitric acid and precipitating the chloride with silver nitrate, the silver chloride being then filtered on a Gooch, dried and weighed.

The following were the results obtained.

Barium Chloride.

<u>BaCl₂·2H₂O</u> <u>weighed</u>	<u>BaCl₂·2H₂O</u> <u>found.</u>	<u>error.</u>
12.45 mg.	12.47 mg.	/ .02 mg.
10.64	10.74	/ .10
12.70	12.63	- .07
.56	.60	/ .04
.68	.66	- .02
10.63	10.70	/ .07
13.90	13.95	/ .05
9.20	9.26	/ .06
21.60	21.57	- .03
16.85	16.75	- .10
4.00	4.04	/ .04
1.46	1.48	/ .02
11.77	11.84	/ .07
43.44	43.52	/ .08
20.56	20.49	- .07
16.45	16.47	/ .02
26.23	26.21	- .02
19.15	19.10	/ .05
.96	.97	/ .01
3.82	3.80	- .02

Sodium Chloride

<u>NaCl</u> <u>Weighed</u>	<u>NaCl</u> <u>found</u>	<u>error.</u>
1.33 mg.	1.34 mg.	/ .01 mg.
5.03	5.02	- .01
5.97	5.95	- .02
3.66	3.62	- .04
7.74	7.80	/ .06
7.14	7.10	- .04
4.40	4.45	/ .05
3.54	3.60	/ .06
2.46	2.53	/ .07
2.50	2.53	/ .03

Lead Chloride

<u>PbCl₂ weighed</u>	<u>PbCl₂ found</u>	<u>error.</u>
5.20 mg.	4.83 m.g.	- .37 mg.
11.98	11.80	- .18
10.00	8.85	-1.15
19.83	19.34	- .49
9.57	9.44	- .13
9.69	9.11	- .58
3.65	4.18	/ .53
4.51	4.26	- .25
1.79	1.78	- .01
9.02	9.84	/ .84 (4 hr. run.)
7.96	8.11	/ .15 " "
29.92	29.72	- .20 " "
4.04	4.81	/ .81 " "

Considering the results with barium chloride we find errors up to .10 mg. Two results out of 20 show an error of .10 mg. while 12 show an error not greater than .05 mg. and 7 out of the 20 not greater than .02 mg. The mean error is .05 mg.

With sodium chloride the greatest error is .07 mg. while 7 out of 10 are not greater than .05 mg. The mean error in this case is .04 mg.

Lead chloride seems to be an exception. Out of 9 results all but 3 show a negative error of from .13 mg. to .58 mg. One of the remaining three is off - 1.15 mg. another one shows a positive of .53 mg. The third is only .01 mg. off. The large amount of error and the fact that 8 out of the 9 were negative indicated that the error was due to the time element. Four were then run for four hours with very unsatisfactory results. At the present time the method as applied to lead chloride is unsatisfactory.

In the case of barium chloride and sodium chloride, an inspection of the results raised the question whether the magnitude of the error could be accounted for by the uncertainty in the end point. Owing to the dilution of the solutions used the end point is uncertain.

M. A. Rosanoff and A. E. Hill found an error of .17% when the AgCl was filtered off. This was with N/10 solutions. With N/100 solutions the error would be increased. To reduce this error as much as possible the plan was adopted of standardizing the ammonium thiocyanate against about the same amount of silver nitrate as there would be excess in the receiving tube to a definite color. Even with this precaution, after the color is once reached it requires several drops of the N/100 ammonium thiocyanate to deepen the color appreciably. It was found better to titrate to the lighter color just after the end point is reached.

In conclusion this method for the determination of very small amounts of chlorine recommends itself by its ease and simplicity. After it is once set up it requires practically no attention during the entire run, thus allowing the chemist to be at other work. As for accuracy, we cannot grant the accuracy claimed by Hulett and Buschak of .01 mg. In the cases of barium chloride and sodium chloride we can claim a minimum accuracy of .07 mg. The method as applied to lead chloride is unsatisfactory. The procedure recommended is the one described in the body of this thesis.

There are many advantages to the method. Other substances except bromides and iodides do not interfere with the determination. This is important as very frequently much time is consumed in removing interfering substances before a determination can be made. The method is applicable to substances insoluble in concentrated sulphuric acid but soluble in either concentrated or dilute nitric acid. First dissolve the substance in nitric acid using as small amount of acid as possible and then introduce into the chamber containing the sulphuric acid. Continue the procedure as usual. The distillation of the nitric acid into the silver nitrate solution produces no injurious effect. Blanks consisting of 15 c.c. con. nitric acid and 15 c.c. con. sulphuric were run to determine the effect upon the receiving solution of silver nitrate. These upon titration with ammonium sulphocyanate gave the same result as the standardization of the silver nitrate. The result was also the same when 15 c.c. 1:1 nitric acid was used. This fact allows the method to be used for solutions as well as solids, since the distillation of any nitric acid along with the HCl does not interfere with the subsequent titration. For extremely small amounts of chlorine such as occluded chloride it is the only method that can be used.

Acknowledgement

I take this means of acknowledging my indebtedness to Prof. J. A. Gibson of the University of Missouri for his suggestion of the problem and his valued assistance.

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AGRICULTURAL EXPERIMENT STATION
DEPARTMENT OF AGRICULTURAL CHEMISTRY

October 9th 1919,

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Academic Hall,
West Campus.

Dear Dean Miller:

I have read the dissertation of Mr. Verner V. Kendall and am of the opinion it is a worthy piece of work carefully carried out. The brevity of the thesis is at first surprising. But this is due to a difference of opinion. Some of us are inclined to think that a thesis has to embody a pretty full discussion of the work and its relation to other work. Others are of the opinion that the explanation and discussion should be as brief as possible and yet present the essentials. I believe this thesis could have been improved by a fuller discussion but I believe that in its present form it does meet the general standard that has been established in this University for the Masters dissertation.

Yours sincerely,

Professor Agricultural Chemistry.

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