

An examination of the hydrazine dichloride, dichlorate and diperchlorate revealed the fact that these salts also are susceptible of titration with solutions of alkali, methyl orange being used as indicator, and of being thereby quantitatively determined, as was shown by Stolle to be the case for the disulfate. Hydrazine diperchlorate also dissolves carbonates with the evolution of carbon dioxide. The dichloride on heating to 180° gives up quantitatively one molecule of its acid,¹ thus resulting in the monochloride. The diperchlorate probably possesses the same property, this surmise being founded on the observation that in a vacuum desiccator and over sulfuric acid the diperchlorate exhibits a marked vapor pressure of perchloric acid, the desiccator becoming filled with the vapor of this acid.

While the pure and dry hydrazine diperchlorate seems to be quite stable, the impure salt, after standing for several months at room temperature, deteriorates, and becomes discolored, assuming a yellow hue. In solution a gradual loss of perchloric acid occurs and crystals of the monopерchlorate form.

The substance, on being struck with a metal hammer, explodes with a loud report.

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[CONTRIBUTION FROM THE HOSPITAL OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH, NEW YORK.]

A METHOD FOR THE TITRATION OF SMALL AMOUNTS OF HALIDES.

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The accuracy, convenience, and wide applicability of the Volhard method for titration of halides has made its use nearly universal. The fact that 1 drop, or about 0.05 cc., of 0.1 *N* solution is required to give the color change satisfactorily at the end point, however, makes it necessary to have under ordinary conditions at least 0.5 milligram molecule of halide, equivalent to 5 cc. of 0.1 *N* silver nitrate, in order that the accuracy of the titration may be within 1%.

The necessity for an accurate means of determining chlorides in small amounts has forced us to seek a titrimetric method with a more sensitive end point, so that less material than is required by the Volhard method may be analyzed with equal percentage accuracy. An iodometric method, with a manipulation almost identical to that of the Volhard titration, proved thoroughly practicable. Like the Volhard, it permits titration in an acid solution, and requires the use only of stable standard solutions, while because of the more sensitive color change it permits one to use

¹ Cartius, *J. prakt. Chem.*, [2] 39, 27 (1889).

0.02 *N* or 0.01 *N* standard solutions and still obtain the end point with one drop. Without sacrificing the accuracy or convenience of the Volhard method, it therefore reduces by about 80% the amount of material required for analysis.

Iodometric determination of chlorides appears to have been first attempted by Pisani,¹ who used a dilute starch-iodine solution to titrate the excess of silver left after precipitation of the chloride with standard silver nitrate solution. Starch-iodine is not stable, however, and consequently the method does not appear to have proven practical. Bang² overcame this disadvantage by utilizing, in place of the starch-iodine, a standard solution of potassium iodide containing a small proportion of potassium iodate. The chloride was precipitated with an excess of standard silver solution containing free nitric acid, the filtrate treated with an excess of the iodide-iodate solution (of about 0.01 *N* conc.), and the excess titrated back with more of the standard silver. A disadvantage of this method is that one can titrate accurately in only one direction; an excess of the iodide-iodate mixture must be added, so that the iodine of all the iodate and of a corresponding amount of iodide is transformed into free iodine ($\text{HIO}_3 + 5\text{HI} = 6\text{I} + 3\text{H}_2\text{O}$). If in titrating one adds the iodine mixture to the silver, the proportion of iodate that is decomposed before the iodide is precipitated depends somewhat on the manner in which the iodine mixture is added, *i. e.*, rate of addition, manner of shaking, etc. It is therefore a drawback that the oxidizing agent used to liberate the iodine of the iodide contains in its own molecule iodine which may also be liberated in the elementary condition. Another drawback to the utilization of the method as described by Bang is the device used to render possible the filtration of the colloidal silver chloride formed in the high dilutions used. The solution containing the precipitate is shaken with kaolin, which adsorbs the silver chloride and gives a clear filtrate. Unfortunately, however, it also adsorbs part of the excess of silver nitrate present. The error introduced by this action was recognized by Bang, who made a correction for it, based on the average amount of silver adsorbed in blank experiments. The necessity for this correction, however, which is not an exact one, makes it impossible to class the method with Volhard's for accuracy. A third disadvantage of Bang's method lies in the titration in the presence of quite concentrated nitric acid, which interferes with the formation of the starch-iodine, and therefore obscures the end point.

The method described below was developed as the result of an attempt to utilize Bang's method. It is similar in principle to the latter (titration with iodide in the presence of an oxidizing agent) but free from the three weaknesses pointed out in the preceding paragraph.

¹ Quoted by Bang, *Biochem. Ztschr.*, 1913, XIX, 33.

² *Loc. cit.*

1. Nitrous, instead of iodic acid, is utilized to free the iodine from the iodide added, so that the possibility of error resulting from incomplete decomposition of iodic acid is eliminated, and one can titrate in either direction. This enables us to simplify the procedure by the elimination of one step, *viz.*: addition of excess of iodide after precipitating the unknown amount of chloride or bromide. As we can now titrate, adding iodide solution to silver, as well as *vice versa*, we need only to filter off the silver bromide or chloride, and titrate the excess of silver in the filtrate directly with standard iodide solution.

2. The use of kaolin or any other adsorbent to make the silver chloride filterable has been rendered unnecessary by utilization of caprylic alcohol to cause coagulation of the colloidal precipitate. This alcohol has a remarkable ability to reduce the surface tension of aqueous solutions, and has been used for some years in this laboratory to prevent foaming of solutions in various operations. Ether has a similar effect of reducing surface tension, although to a less marked extent, and Rothmund and Burgstaller¹ showed that shaking a solution of colloidal silver chloride with ether accelerated the coagulation in the Volhard procedure. Ether did not prove practicable in our case, for its presence interfered with the sensitiveness of the end reaction. Caprylic alcohol, however, is even more efficient, and does not interfere. One adds two or three drops of the alcohol to the solution containing freshly precipitated silver chloride or bromide and shakes vigorously for a few seconds. This treatment coagulates the precipitate to such an extent that it can be collected on an ordinary folded filter, and gives a perfectly clear filtrate. The first few drops that pass through a dry filter are sometimes cloudy, but if they are passed through a second time a clear filtrate is obtained. In fact the filtrates we usually obtained from a silver chloride coagulated with caprylic alcohol were so clear that the turbidity determined with Richard's nephelometer exceeded to a barely detectable degree that of the silver nitrate solution in the dilution used.² In control tests with the nephelometer we could detect 0.1 mg. of NaCl added to a slight excess of silver solution in a liter of water.

3. The addition of a "buffer salt" is utilized in order to give the slight degree of acidity necessary for the sharpest end point. In most cases it is convenient or necessary to precipitate the silver halide in nitric acid solution. When the excess of silver is titrated back with iodide, the presence of free nitric acid in even moderate concentration seriously interferes with the end point. The starch does not, until a considerable excess of iodine is present, combine appreciably with it in strongly acid

¹ *Z. anorg. Chem.*, 63, 330 (1909).

² Caprylic alcohol can also be used to advantage in gravimetric determination of chlorides to facilitate coagulation of the silver chloride.

solution, and consequently the end point obtained is the yellow-brown color of free iodine, which is much more difficult to detect than the blue of the starch compound. The difficulty is obviated by adding an amount of trisodium citrate, equivalent to the free nitric acid present, before the titration is begun. The amount added may vary 10% above or below an exact equivalent without affecting the end point. A solution containing one molecule of potassium acetate to three of acetic acid may also be used, but the citrate solution appears to give the clearer end point.

Description of the Method.

The halide is precipitated in the presence of a known amount of free nitric acid, preferably about one gram, with an excess of 0.04 *N* or 0.02 *N* standard silver nitrate solution. In the case of bromides and chlorides the silver halide is removed by filtration, after coagulation of the colloid precipitate has been accomplished by shaking the mixture for a few seconds with one or two drops of caprylic alcohol. In case a dry filter is used it may be necessary to pass the first portion of the filtrate through a second time in order to make it perfectly clear.

In either the entire filtrate, washed through the filter, or in an aliquot part, passed through a dry filter, the excess of silver is titrated with 0.02 *N* or 0.01 *N* potassium iodide, which has been standardized against the silver solution.¹ Just before titration one adds from a buret for each gram of free nitric acid present (one gram approximately, or 16 mg. molecules, is contained in 1 cc. of nitric acid of 1.42 specific gravity) 4 cc. of the following solution:

| | | |
|---|------------|---|
| Trisodium citrate, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 + 5\frac{1}{2}\text{H}_2\text{O}$ | 446.0 g. | } 5/4 gram-molecules or 15/4 equivalents |
| Sodium nitrite..... | 19.0 | |
| Soluble starch..... | 2.5 | |
| Water to..... | 1000.0 cc. | |

One cc. of this solution contains four milligram-equivalents of sodium. The solution, because of its nitrite, serves to liberate iodine; the citrate regulates the acidity of the titrated solution; and the starch is present for the end reaction. Under the above conditions one obtains, with one drop of 0.02 *N* iodide, a very sharp color change, that can be seen in 150 cc. of solution, and is, of course, still more striking in a smaller volume. It is preferable, though not necessary, to keep the volume of the filtrate to be titrated within 50 cc.

The removal, by filtration, of silver chloride or bromide before titrating back with iodide is necessary, because iodine forms a much more insoluble silver salt than either of the other halogens. It reacts with their precipi-

¹ The accuracy of the silver nitrate solution can be checked by titration against 0.01 *N* or 0.02 *N* hydrochloric acid prepared from redistilled acid by the method of Hulett and Bonner, *THIS JOURNAL*, 31, 390 (1909).

tates ($\text{AgCl} + \text{HI} = \text{AgI} + \text{HCl}$) so rapidly that the slight amount of iodine necessary to give the end point is removed from solution in a few seconds by freshly precipitated silver chloride or bromide. This is true for both chlorides and bromides in strongly acid solution. When the acidity is depressed by the addition of sodium citrate as described above, the change still occurs so rapidly with chlorides that no end point with iodide can be obtained. In the case of bromides a sharp end point is obtained that persists for a short time. The amount of iodide necessary to produce this end point is slightly in excess of the correct amount, so that in order to obtain exact results filtration of the bromide precipitate also is necessary (Tables III and IV). When, in either case, the titration is performed after removal of the silver halide precipitate, the end point produced with one drop of excess of iodide lasts for hours, and in fact seems to intensify with time. For reasons similar to the above, *i. e.*, the relative insolubility of silver thiocyanate compared with silver chloride, it is necessary to remove the silver chloride in the Volhard titration in order to obtain the most satisfactory results.¹ Filtration is, of course, unnecessary in the determination of iodides by our method.

Experimental.

Our standard solutions were based on: (1) the constant boiling hydrochloric acid described by Hulett and Bonner² and (2) special "Reagent" metallic silver, which was dissolved in a slight excess of nitric acid. Hulett and Bonner claim a composition constant within one part in 10,000 for the acid distilled by their method, and we have in several years' use of it never found an appreciable variation from their values. The solution used in this case was distilled at 760 mm. atmospheric pressure, so that, according to Hulett and Bonner's table, 180.17 g. contained one gram molecule of HCl.³ The standard solutions made by weight from this acid and from the "Reagent" silver foil checked each other within one part per thousand when titrated by Volhard's method, with filtration of the silver chloride.

The bromide solutions were made by weight from pure potassium bromide, and standardized by careful titration against the silver solution by Volhard's method. As there was no detectible impurity, the salt was not recrystallized.

The potassium iodide solution used was of $M/58.5$ concentration. It was prepared originally for determination of sodium chloride (1 cc. $M/58.5$ NaCl = 1 mg.) and standardized by titration against the silver solutions.

¹ See Rosanoff and Hill, *THIS JOURNAL*, 29, 269 (1907), and Rothmund and Burgstaller, *Z. anorg. Chem.*, 63, 330 (1909).

² *Loc. cit.*

³ Gravimetric determinations gave the following results: 2.1802 g. HCl solution, 1.7350 g. AgCl; 2.1792 g. HCl, 1.7348 g. AgCl; g. HCl solution calculated to contain 36.46 g. of HCl, 180.17 and 180.12.

For the determinations of Tables I and III the precipitated and coagulated chloride or bromide was washed several times by decantation, then several times on the filter, with water at room temperature, and the entire filtrate was titrated. For Table II aliquot parts were taken, as indicated.

TABLE I.—DETERMINATIONS ON KNOWN AMOUNTS OF CHLORIDE. TOTAL FILTRATES, WASHED QUANTITATIVELY.

| Cc. HCl. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Cl found. | Mg. Cl present. | Error. Mg. Cl. | Error. Per cent. |
|------------|-------------------------|----------------|---------------|-----------------|----------------|------------------|
| 1.00 N/50 | 1.00 N/29.25 | 0.82 | 0.715 | 0.709 | +0.006 | +0.8 |
| 1.00 | 1.00 | 0.85 | 0.697 | 0.709 | -0.012 | -1.7 |
| 2.00 | 2.00 | 1.65 | 1.425 | 1.418 | +0.007 | +0.5 |
| 2.00 | 2.00 | 1.66 | 1.418 | 1.418 | 0.000 | 0.0 |
| 5.00 | 5.00 | 4.17 | 3.532 | 3.546 | -0.014 | -0.4 |
| 5.00 | 5.00 | 4.15 | 3.546 | 3.546 | 0.000 | 0.0 |
| 10.00 | 7.00 | 2.30 | 7.092 | 7.092 | 0.000 | 0.0 |
| 10.00 | 7.00 | 2.32 | 7.076 | 7.092 | -0.016 | -0.23 |
| 25.00 | 15.00 | 0.73 | 17.74 | 17.730 | +0.010 | +0.06 |
| 25.00 | 15.00 | 0.80 | 17.70 | 17.730 | -0.030 | -0.17 |
| 20.00 N/14 | 20.00 N/10 | 33.30 | 50.73 | 50.657 | +0.073 | +0.14 |
| 20.00 | 20.00 | 33.40 | 50.67 | 50.657 | +0.013 | +0.025 |
| 20.00 N/10 | 22.00 | 11.83 | 70.84 | 70.920 | -0.079 | -0.11 |
| 20.00 N/10 | 22.00 | 11.82 | 70.85 | 70.920 | -0.073 | -0.10 |

TABLE II.—DETERMINATIONS ON KNOWN AMOUNTS OF CHLORIDE. VOLUME MADE TO 25 CC. FILTERED THROUGH DRY FILTER AND 20 CC. OF FILTRATE TAKEN FOR TITRATION.

| Amt. HCl. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Cl found. | Mg. Cl present. | Error. Mg. Cl. | Error. Per cent. |
|------------|-------------------------|----------------|---------------|-----------------|----------------|------------------|
| 1.00 N/50 | 1.00 N/29.5 | 0.68 | 0.697 | 0.709 | -0.008 | -1.1 |
| 1.00 | 1.00 | 0.70 | 0.688 | 0.709 | -0.021 | -3.0 |
| 5.00 | 5.00 | 3.35 | 3.521 | 3.546 | -0.025 | -0.7 |
| 5.00 | 5.00 | 3.31 | 3.555 | 3.546 | +0.007 | +0.2 |
| 10.00 | 7.00 | 1.85 | 7.086 | 7.092 | -0.006 | -0.08 |
| 10.00 | 7.00 | 1.82 | 7.014 | 7.092 | +0.012 | +0.17 |
| 20.00 N/10 | 21.00 N/10 | 5.98 | 70.82 | 70.92 | -0.10 | -0.14 |
| 20.00 | 22.00 | 11.53 | 71.02 | 70.92 | +0.10 | +0.13 |

TABLE III.—DETERMINATIONS ON KNOWN AMOUNTS OF BROMIDE. TOTAL FILTRATES, WASHED QUANTITATIVELY.

| Solution of KBr. 1 cc. = 0.994 Mg. KBr and 0.667 Mg. Br. | | | | | | |
|--|-------------------------|----------------|---------------|-----------------|----------------|------------------|
| Cc. of KBr sol. | Cc. AgNO ₃ . | Cc. N/58.5 KI. | Mg. Br found. | Mg. Br present. | Error. Mg. Br. | Error. Per cent. |
| 4.000 | 2.00 N/29.25 | 2.04 | 2.675 | 2.668 | +0.007 | +0.26 |
| 4.000 | 2.00 | 2.00 | 2.730 | 2.668 | +0.062 | +2.3 |
| 5.000 | 2.00 | 1.55 | 3.345 | 3.335 | +0.010 | +0.3 |
| 5.000 | 2.00 | 1.55 | 3.345 | 3.335 | +0.010 | +0.3 |
| 7.000 | 3.00 | 2.60 | 4.640 | 4.669 | -0.029 | -0.62 |
| 7.000 | 3.00 | 2.62 | 4.613 | 4.669 | -0.056 | -1.20 |
| 25.000 | 7.00 | 1.73 | 16.74 | 16.69 | +0.05 | +0.30 |
| 25.000 | 7.00 | 1.75 | 16.72 | 16.69 | +0.03 | +0.18 |
| 50.174 | 5.00 N/10 | 4.78 | 33.43 | 33.43 | 0.000 | =0.00 |
| 50.174 | 5.00 | 4.75 | 33.47 | 33.43 | +0.04 | +0.11 |

In the bromide determinations of Table IV the silver bromide was not filtered off, and the iodide titration was performed in its presence. It will be seen that under these conditions an error of 1-2% must be allowed for, because of the reaction between HI and AgBr already discussed.

TABLE IV.—DETERMINATIONS ON KNOWN AMOUNTS OF BROMIDE. TITRATION PERFORMED IN PRESENCE OF AgBr PRECIPITATE.

| Cc. KBr solution (1 cc. = 0.667 mg. Br). | Cc. $N/29.25$ $AgNO_3$. | Cc. $N/58.5$ KI. | Mg. Br found. | Mg. Br present. | Error, Mg. Br. | Error, Per cent. |
|--|--------------------------|------------------|---------------|-----------------|----------------|------------------|
| 4.00 | 2.00 | 2.08 | 2.620 | 2.668 | -0.048 | -1.8 |
| 4.00 | 2.00 | 2.10 | 2.593 | 2.668 | -0.075 | -2.8 |
| 5.00 | 2.00 | 1.58 | 3.305 | 3.335 | -0.030 | -0.9 |
| 5.00 | 2.00 | 1.58 | 3.305 | 3.335 | -0.030 | -0.9 |
| 10.00 | 4.00 | 3.18 | 6.580 | 6.670 | -0.090 | -1.35 |
| 10.00 | 4.00 | 3.20 | 6.555 | 6.670 | -0.115 | -1.70 |
| 25.00 | 7.00 | 2.10 | 16.250 | 16.690 | -0.440 | -2.6 |
| 25.00 | 7.00 | 1.92 | 16.500 | 16.690 | -0.190 | -1.1 |

From inspection of Tables I, II and III it will be seen that the titration error exceeds 0.05 cc. (1 drop) of the $M/58.5$ KI solution, equivalent to 0.03 mg. Cl or 0.07 mg. Br, only when the amounts titrated are so large that this error falls within or near the 1 pro mille limit. In most cases where small amounts were analyzed, the results indicate that the absolute error was within half a drop.

The percentage error ranges from a maximum of 3% in analyses of the smallest amounts, 0.7 mg. Cl and 2.6 mg. Br, down to 0.1% towards the other end of the scale, where amounts up to 70 mg. of Cl and 33 mg. of Br were determined.

Summary.

A method for titration of halides is described which permits utilization of the starch-iodine color for the end point. Because of the sensitiveness of the color change under the conditions ascertained, and the simplicity of the manipulation, amounts of halide no greater than 0.5 mg. molecule can be determined with an accuracy of one part per thousand.

THE OXIDATION OF SULFIDES WITH POTASSIUM IODATE.

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L. W. Andrews¹ has shown that in solutions containing 50% by volume, or more, of concentrated hydrochloric acid at the end of the titration, potassium iodate may be used as an oxidizing agent, and that under such conditions the iodine, which is at first liberated by the reduction of iodate, is finally completely converted into iodine chloride, ICl, and the end of the titration can be shown by the disappearance of the iodine color in

¹ THIS JOURNAL, 25, 756 (1903).