platinic acid gave precipitates with 11% ammonium chloride, 1.92% rubidium sulfate and 1.16% cesium sulfate solutions as well as with 8.8% potassium sulfate solution. Perchloric acid gave a precipitate with the same solutions except the 1.16% cesium sulfate solution, but when a more concentrated cesium sulfate solution was prepared, it gave an immediate precipitate. *Zirconium sulfate gave a precipitate with the 8.8% potassium sulfate solution only.*

Reagents for the detection of potassium, other than zirconium sulfate, cannot be used in the presence of all members of the fifth group of metals. Sodium cobaltic nitrite, perchloric acid and chloroplatinic acid give a precipitate with rubidium and cesium as well as with potassium and ammonium. The perchloric acid method requires the use of absolute alcohol and the chloroplatinic acid requires the use of 80% alcohol to separate potassium from sodium and lithium.

Summary

Zirconium sulfate will detect 1.0 mg. or more of potassium in 2 cc. of reaction mixture in the presence of lithium, rubidium, cesium or magnesium ions, as well as those of sodium and ammonium. The detection of potassium by zirconium sulfate is accomplished without the use of alcohol or complicated procedure. It should always be used as the preliminary reagent, therefore, in looking for potassium, before going through the ordinary more complicated procedure.

COLUMBUS, OHIO

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

A STUDY OF THE DETERMINATION OF CHLORIDE IN BROMIDES

BY R. K. MCALPINE

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In 1926 Berg[1] introduced an interesting modification of the usual procedure for determining chloride in the presence of bromide by using acetone in aqueous solution to absorb the bromine set free in a differential oxidation process that employed potassium bromate in dilute sulfuric acid solution. The following equation shows the reaction involved:

$$6CH_3COCH_3 + 2KBrO_3 + 4KBr + 3H_2SO_4 = 6CH_3COCH_2Br + 3K_2SO_4 + 6H_2O$$

The chloride was then titrated by a modification of the Volhard method. The experimental data in Berg's article showed that the procedure recommended worked within moderate limits and it was suggested that the nephelometer could be used to determine very small amounts of chloride.

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[1] Berg, *Z. anal. Chem.*, **64**, 342 (1926).

The present work was undertaken to replace potassium bromate with potassium permanganate and to extend the usefulness of the procedure in determining small amounts of chloride in bromides. Potassium permanganate has several advantages as an oxidizing agent. It is inexpensive, readily obtained free from halide, highly colored so that excess is easy to recognize, and easily reduced by hydrogen peroxide so the excess is simple to destroy.

Two general errors are possible in such work; one, incomplete removal of the bromide, leading to high results; the other, loss of chloride, leading to low results. Correct figures might be obtained by reducing both errors to negligible magnitude or from compensation of the two.

In the present work the chloride was determined gravimetrically, since such a precipitate could then be examined for bromide. The silver chloride was collected on a Jena filtering crucible, the weight of which is not affected by more than one or two-tenths of a milligram by the ordinary processes of filtering and washing. At the balance the more accurate procedure was adopted of using a counterpoise and weighing by substitution. This method of weighing easily reduces the ordinary error of four or five-tenths of a milligram to one-tenth of a milligram.

There were available as materials for study several commercial bromides of sodium and potassium and two specimens of potassium bromide of a high degree of purity. One of the latter had been prepared in connection with earlier work in the Laboratory[2] from recrystallized potassium oxalate and purified bromine; the other was made from Kahlbaum's potassium bromate that had been further purified by several recrystallizations using centrifugal drainage of the crystals. The potassium bromate was converted to bromide by careful heating in an electric furnace. A standard chloride solution was prepared from very pure sodium chloride, the concentration being determined by precipitation as silver chloride.

The accessory reagents used included potassium permanganate, sulfuric acid, nitric acid, silver nitrate, manganous sulfate, acetone, ether and hydrogen peroxide. Commercially available preparations were selected that were found on test to be either free from halide or to contain so small an amount that the total error for all combined would not exceed a tenth of a milligram. In the case of hydrogen peroxide, Merck's "Perhydrol" was used, being diluted to one-tenth its concentration and stabilized with diluted sulfuric acid.

Analytical Procedures

The analytical studies carried out may be divided into three general groups: (I) the use of permanganate in moderate excess in slightly acid solution, (II) the use of permanganate in slight excess in strongly acid

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[2] Willard and McAlpine, THIS JOURNAL, **43,** 797 (1921).

solution and (III) the development of a concentration method for working with larger samples.

(I) The use of permanganate in slightly acid solution. The procedure first tried was patterned after that developed by Berg, using a moderate excess of potassium permanganate in relatively low acidities and with a large excess of acetone to react with the bromine. The reactions were carried out in a half-liter, glass-stoppered Erlenmeyer flask so that the final solution after addition of the silver nitrate could be shaken vigorously to coagulate the precipitate. Five ml. each of nitric acid (1:1) and of ether were added to assist this process.

By separate experiments with potassium bromide and sodium chloride solutions (see Table I) conditions were worked out such that the bromine from 50 mg. of potassium bromide could be converted completely to bromo-acetone and that 100 mg. of chlorine as chloride would suffer only the negligible loss of three- or four-tenths of a milligram. A quantitative determination of chloride in such a synthetic mixture gave a result containing no measurable error.

TABLE I

DETERMINATIONS OF CHLORIDE USING A MODERATE EXCESS OF POTASSIUM PERMANGANATE IN SLIGHTLY ACID SOLUTION

H_2SO_4 added		Acetone			Time before reduction,	Error calcd.
Vol., ml.	Concn., N	ml.	KBr, g.	Cl^-, g.	min.	as Cl^-, g.
50	1.5	25	0.050	0.00	2	+0.0007
50	1.5	25	.050	.00	5	.0000
50	2.0	25	.050	.00	2	.0000
50	2.5	25	.050	.00	2	.0000
50	1.5	25	.00	.1001	2	− .0003
50	1.5	25	.00	.1001	5	− .0004
50	1.5	25	.00	.0100	2	− .0001
50	1.5	25	.00	.0501	2	− .0002
50	1.5	25	.00	.2503	2	− .0006
50	2.5	25	.00	.0100	5	− .0004
50	2.5	25	.00	.0501	5	− .0005
50	2.5	25	.00	.2503	5	− .0011
50	1.5	25	.050	.1001	5	.0000

The directions worked out for the last determination in Table I were as follows. Use 25 ml. of acetone and 50 ml. of 1.5 N sulfuric acid in a total volume of approximately 85 ml. Add dropwise a 5% solution of potassium permanganate until the characteristic color persists, then 15 to 20 drops in excess. Let the solution stand for five minutes, reduce with 2 ml. of the hydrogen peroxide solution, add 5 ml. of nitric acid (1:1) and 5 ml. of ether, precipitate with silver nitrate, filter, wash with 1% nitric acid, dry and weigh.

On increasing the sample of potassium bromide to one gram the results of this method were not satisfactory. Qualitatively the reaction started smoothly with immediate decolorization of the permanganate and production of a yellow color of bromine that disappeared as the reaction with acetone took place; hydrated manganese dioxide soon started to precipitate and from then on the decolorization proceeded more and more slowly. The time required for disappearance of color when five drops of the reagent were added lengthened to one, two and even five minutes. At the latter stage the oxidation of the bromide was still far from complete. By continued addition of permanganate the test for bromide became faint, but by that time half an hour or more had been consumed with this operation. Even then quantitative tests showed that with 1 g. of potassium bromide and 100 mg. of chloride, the final precipitate gave a distinct test for bromide and yet its weight corresponded to a loss of over one milligram of chloride.

Further studies in dilute acid solution were therefore abandoned and the work entered its second phase.

(II) The use of permanganate in strongly acid solution. Since the oxidation potential of permanganate ion increases distinctly with the acidity of the solution, it seemed probable that conditions could be found such that with only a slight excess of permanganate the bromide would be completely changed to bromo-acetone without appreciable loss of chloride.

Test experiments showed that with increasing acidity, ranging from 3 to 10 *N* sulfuric acid, the volume of permanganate solution that was decolorized promptly by half a gram of potassium bromide increased very appreciably. At the same time precipitation of hydrated manganese dioxide decreased, finally ceasing entirely, and the color at the end-point became more definitely that of a dilute permanganate solution. These differences were distinct arguments in favor of using these newer conditions providing (a) the bromide was thus completely converted to bromo-acetone, (b) the chloride was not attacked, (c) the end-point

TABLE II

PERMANENCE OF THE PERMANGANATE END-POINT

H_2SO_4 (1:1), ml.	Solution tested $MnSO_4$ 0.3 *N* ml.	Acetone, ml.	Bromide added, g.	Chloride added, g.	$KMnO_4$ added, 5% soln.	Duration of color
50	0.0	25	0.0	0.0	1 drop	Permanent[a]
50	10.0	25	.0	.0	1 drop	Permanent[a]
50	0.0	25	.0	.10	1 drop	20 sec.
50	10.0	25	.0	.10	1 drop	5 min.
50	10.0	25	.0	.01	1 drop	18 min.
50	10.0	25	.05	.00	1.28 ml.	15 min.
50	10.0	25	.05	.01	1.30 ml.	10 min.

[a] In using the word permanent in this connection it should be noted that while one drop of the permanganate solution in 85 ml. produced a deep color in water alone, the color in these cases shifted rapidly to a light pink—deeper with manganous sulfate present than without—but when this light stage was once reached it did not undergo further change over a period of several minutes.

was reasonably permanent and, finally, (d) that the chloride could be quantitatively precipitated from such a solution. Quantitative experiments showed that these conditions were all fulfilled when one important modification was introduced, namely, the addition of 10 ml. of 0.3 *N* manganous sulfate solution to inhibit the oxidation of the chloride. In Table II are given data showing the satisfactory character of the end-point with manganous sulfate present.

The following quantitative procedure was finally adopted: measure out the volume of concentrated bromide solution to be analyzed, add 25 ml. of acetone, 10 ml. of 0.3 *N* manganous sulfate solution and 50 ml. of (1:1) sulfuric acid, cool in running water to 15–20°, add 5% potassium permanganate solution slowly with swirling until an end-point is reached, then add sufficient sulfuric acid to make the solution 11–11.5 *N* with respect to the acid, cool again and titrate to an end-point. Add one drop extra of the permanganate solution, let stand for one and a half to two minutes, reduce with a few drops of hydrogen peroxide, add ether and nitric acid as usual, precipitate with 0.25 *N* silver nitrate, adding 4 ml. excess, shake for one minute, filter, wash, dry and weigh.

Typical determinations using this procedure are given in Table III.

TABLE III

DETERMINATIONS OF CHLORIDE USING A SLIGHT EXCESS OF PERMANGANATE IN STRONGLY ACID SOLUTION

(a) Synthetic Mixtures

KBr taken, g.	Chloride added, g.	Error calcd. as chloride, g.	Bromide test on ppt.
0.10	0.010	0.0000	..
.10	.020	− .0001	Neg.
.10	.050	− .0006	..
.10	.100	− .0008	Neg.
.50	.00	+ .0005	..
.50	.00	.0000	..
.50	.001	+ .0002	Neg.
1.00	.001	+ .0011	Pos.

(b) Commercial Salts

Salt	Sample no.	Wt. of sample, g.	Chloride found, %	Bromide test on ppt.
NaBr	1	0.500	1.00	Neg.
NaBr	1	1.000	1.10	Pos.
NaBr	1	1.000	1.05	Neg.
NaBr	2	0.500	0.69	Pos.
NaBr	3	.500	.29	Pos.
KBr	4	.500	.38	Pos.
KBr	5	.500	.40	Pos.

Preliminary quantitative experiments during the development of the above procedure using amounts of potassium bromide ranging from 50 mg. to 1 g. and with chloride added in quantities ranging from 1–200 mg. gave a maximum negative error of 2.4 mg. and a maximum positive error of 3 mg., calculated as chloride. The negative error was cut down by cooling the solution more carefully and the positive error was decreased by adding the extra drop of permanganate solution and letting stand a minute longer before reducing. With the procedure thus modified the errors on a 1-g. sample were found to lie within ±1 mg., an accuracy of 0.1%.

The work with half-gram and gram samples indicated that the rate of hydrolysis of the bromo-acetone might increase sufficiently with higher concentrations to offset any gain in accuracy that a larger sample might be expected to give. To show this more definitely two solutions of bromo-acetone of differing concentrations were prepared. Treatment with silver nitrate showed that silver bromide did precipitate more readily from the solution of higher concentration. Further, the rate of precipitation was not affected by an increase in the excess of acetone from ten-fold to two hundred and fifty-fold. In both solutions, however, the rate was decreased by an increase in acidity, falling off in one case to one-fifth by a change from 0.16 to 10 *N*, and in the other case to one-third by a change from approximately 2.6 to 11 *N*. The readiness with which opalescence developed even in the latter solution made it evident that the use of the nephelometer to determine small amounts of chloride could be of only limited value. Accordingly it was clear that an increase in accuracy would require a concentration method whereby most of the bromine could be removed before the acetone was added.

(III) Development of a concentration method. In removing most of the bromine by permanganate oxidation and direct volatilization it must be remembered that only half as much permanganate is required to convert bromide to free bromine as to change it to bromo-acetone. This is shown in the following equations

$$2KMnO_4 + 10KBr + 8H_2SO_4 = 5Br_2 + 6K_2SO_4 + 2MnSO_4 + 8H_2O \qquad (1)$$

$$4KMnO_4 + 10KBr + 10CH_3COCH_3 + 11H_2SO_4 = 10CH_3COCH_2Br + 4MnSO_4 + 7K_2SO_4 + 16H_2O \qquad (2)$$

In preliminary experiments there was added an amount of the 5% potassium permanganate solution that left about 0.2 g. of bromide unoxidized. The flask was then left on the edge of the hot-plate until the color became light yellow, cooled, treated with acetone and the rest of the operation carried out as before.

With 10-g. samples the final process of filtering out the silver chloride became slow. This was aggravated by the fact that the acetone interfered with the usual coagulation of a small precipitate so that the latter would occasionally mat in the filtering crucible and clog it seriously. This difficulty had been encountered in earlier work and largely overcome by using regulated suction such that the first filtering was complete in three to eight minutes. To reduce the volume sufficiently so that the same time range could be used here it was only necessary to substitute solid potassium permanganate for the solution and to use limited amounts of water, thus keeping the final volume within 100 ml. Since the mechanical difficulty referred to became evident only in the case of very small precipitates, one could eliminate it by adding a definite amount of chloride immediately before precipitating with silver nitrate. The final weight of precipitate could then be corrected for the amount of chloride added. This modification was regularly introduced when determining the small amounts of chloride that might be present in high grade analytical reagents.

Larger samples than 10 g. were not used because even with this amount salts frequently crystallized out when the acetone was added and the solution cooled. In such cases the salt redissolved when the precipitate was washed but the filtrate was usually cloudy and required refiltration.

A further source of error lay in the possible loss by volatilization of hydrogen chloride in the heating used to remove the bromine. Quantitative studies showed that with 100 mg. of chloride present and 50 ml. of (1:1) sulfuric acid, standing on the edge of the hot plate for one hour caused considerable loss of chloride. With smaller amounts of chloride the loss decreased and with the acidity lowered to 50 ml. of (1:3) sulfuric acid the loss became negligible.

The following is the procedure recommended for the concentration method: weigh out 10 g. of the bromide and 0.1 g. less than an equivalent amount of potassium permanganate (as calculated from Equation 1), transfer to a half-liter, glass-stoppered Erlenmeyer flask, add 40 ml. of water and 10 ml. of 0.3 N manganous sulfate solution and swirl for one or two minutes to dissolve the salts. Add 25 ml. of (1:1) sulfuric acid and place on the edge of the hot plate until the solution becomes light yellow (thirty to fifty minutes). Cool, add 10 ml. of acetone and sufficient sulfuric acid to make the solution 11 to 11:5 N with respect to the acid, cool again to 15–20° and treat dropwise with a 5% solution of potassium permanganate until one drop gives a permanent pink color. Add one drop more, let stand for one to two minutes, insert a tube into the flask above the solution and blow out any slight bromine vapors present; then reduce with a few drops of diluted Perhydrol solution. Add a measured volume of standard sodium chloride solution (20 mg. of chlorine), 5 ml. each of ether and of (1:1) nitric acid and precipitate with 0.25 N silver nitrate solution. Swirl the solution while the latter reagent is run in slowly until the solution shows a distinct decrease in opalescence, then add 4 ml. more of the reagent. Insert the stopper, shake for one minute, cool (to avoid loss when removing stopper), transfer the precipitate to a weighed filtering crucible, wash with 1% nitric acid, dry for three hours at 130°, cool and weigh. From the weight found subtract the weight corresponding to the amount of chloride added and calculate the percentage of chloride.

Typical determinations using this procedure are given in Table IV.

TABLE IV

ANALYSES OF BROMIDES BY THE PRELIMINARY CONCENTRATION METHOD

Salt analyzed	Wt. of sample, g.	Chloride found, %	Bromide test on ppt.
Best comml. NaBr	10.0	0.190	Slight[a]
Best comml. NaBr	10.0	.190	Faint
Best comml. NaBr	10.0	.189	Faint
Special KBr[b]	4.0	.014	Faint
Special KBr	8.0	.010	Faint

[a] Studies of known bromide–chloride mixtures showed that the precipitatt with silver nitrate gave a recognizable test for bromide with as low as 0.2 mg. of bromine. In testing for bromide the precipitate in the crucible was treated with a little water, plus a few drops of sulfuric acid and several tenths of a gram of granular zinc. After standing for four or five minutes the solution was filtered and the filtrate tested by adding a little more sulfuric acid, one or two drops of permanganate solution and then shaking out with carbon tetrachloride.

[b] This salt was the material prepared from potassium oxalate and bromine as earlier described.

Magnitude of Errors in the Final Procedure.—The positive error due to inclusion of silver bromide in the final precipitate might be caused by incomplete oxidation of the bromide or by partial hydrolysis of the bromo-acetone. The material presented in Table II (last two lines) showing the permanence of the permanganate end-point indicates that the bromide must be completely oxidized. It has already been shown that a bromo-acetone solution reacts slowly with silver nitrate but from the work done it would appear that this reaction was not sufficient to account for the slight tests for bromide obtained in the latter part of this study. In the precipitation of silver chloride, however, it would be possible for more silver bromide to be carried down than might separate from the solution by itself.

This point was tested experimentally by preparing a solution containing a little over 0.3 g. of bromine as bromo-acetone, adding 100 mg. of chloride and then, with other conditions the same as in the above determinations, the chloride was precipitated with silver nitrate. An excess weight was obtained corresponding to 0.6 mg. of bromine carried down. This amount would be sufficient to account for the bromide tests since examination of the method used in testing the precipitates showed it to be capable of recognizing as little as 0.2 mg. of bromine. The excess weight of the precipitate calculated as chloride would introduce an error of only 0.4 mg., and since the amount of bromo-acetone used was greater than would commonly be present at the end of the concentration method, this figure would appear to be a maximum for this error.

Loss of chlorine by volatilization of hydrogen chloride had already been reduced to negligible magnitude by control of the acidity during removal of the bromine. To determine directly the extent of oxidation by permanganate under the final conditions two test experiments were run. One hundred milligrams of chloride in a solution prepared as for a regular determination lost 0.4 mg. of chlorine on treatment at room temperature (22°) with one drop of 5% permanganate solution and letting stand for one and a half minutes before reduction. The second solution, cooled to 15°, was treated with two drops of the permanganate solution and let stand for two minutes before reduction. The loss this time was only 0.5 mg. This loss may be taken as a maximum when small quantities of chloride are to be determined, for in such cases one would never be dealing with as much chloride as was present in these experiments.

The errors of the method as finally developed may, therefore, be considered to lie within the limits of ±0.5 mg. and to be compensating in character.

Summary

1. A method has been worked out for the determination of chloride n bromides using potassium permanganate and acetone to convert the

bromide to bromo-acetone. The chloride is then determined gravimetrically as silver chloride.

2. The various errors of the process have been carefully studied.
3. On a 1-g. sample the accuracy of the procedure lies within 0.1%.
4. The rate at which a solution of bromo-acetone reacts with silver nitrate makes the nephelometric method inaccurate for small amounts of chloride.
5. By using a preliminary concentration method samples up to 10 g. can be employed for the accurate analytical testing of high grade reagents.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE TRANSFERENCE NUMBER OF BARIUM CHLORIDE AS A FUNCTION OF THE CONCENTRATION

BY GRINNELL JONES AND MALCOLM DOLE

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Introduction

According to the classical electrolytic dissociation theory of Arrhenius the transference number of the ions should be independent of the concentration, but there are numerous well-established exceptions to the old rule. It has been the common practice to explain away the known variation of the transference number with the concentration as due to the presence of complex ions or as due to hydration in amounts which vary with the concentration, but these speculations have as a rule been qualitative only, with little serious attempt to develop a consistent quantitative theory or to express the variation of the transference number quantitatively as a function of the concentration.

The newer theory of complete electrolytic dissociation of Debye and Hückel gives a new point of view for the study of transference numbers. The new theory, unlike the old, does not neglect the electrostatic forces between the ions. According to this theory, at finite concentrations, the interionic forces tend to maintain a space lattice distribution of the ions and to oppose any disturbance of this arrangement by an outside electric field from an electrode and thus decrease the mobility of the ions. Therefore, the velocity of motion of an ion is not proportional to the potential gradient due to the outside electrode alone regardless of the concentration but is a decreasing function of the concentration. Debye and Hückel[1] have derived from this standpoint an equation for the variation of the equivalent conductance of strong electrolytes as a function of the concentration. This equation fits the facts fairly well at extreme dilutions

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[1] P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923); **24**, 305 (1923); E. Hückel, *Ergebnisse der Exakten Naturwissenschaften*, **3**, 199 (1924).