169. *Improved Methods for the Separation of Chloride from Bromide by Means of Ammonia.*

By Thomas B. Smith.

An examination of the method of detecting chlorion in the presence of bromion, based upon the greater solubility of silver chloride in aqueous ammonia, shows that it is untrustworthy in its usual form. Since a trace of silver bromide invariably dissolves, it is difficult to be certain whether chloride is present or not if the turbidity is only slight, and even when the proportion of chloride is large, the amount of precipitate finally obtained may vary widely with slight changes in the experimental procedure. By modifications now to be described, however, it is possible, not only to obtain reliable indications as to quantity, but also to detect 0·002 mg. of chlorion in the presence of 100 mg. of bromion.

Defects of the Old Method.—Many of the difficulties of this method can be elucidated by a consideration of the equilibria involved. It will suffice to make use of the following approximate relations for a temperature of 15° :

$$\text{Solubility product of AgCl, } S_{\mathrm{p,AgCl}} = [\mathrm{Ag}^{\cdot}][\mathrm{Cl}'] = 8{\cdot}5 \times 10^{-11}\,{}^{*} \quad . \quad . \quad . \quad . \qquad \text{(i)}$$

$$\text{Solubility product of AgBr, } S_{\mathrm{p,AgBr}} = [\mathrm{Ag}^{\cdot}][\mathrm{Br}'] = 1{\cdot}7 \times 10^{-13}\,{}^{\dagger} \quad . \quad . \quad . \quad . \qquad \text{(ii)}$$

$$[\mathrm{Ag}^{\cdot}][\mathrm{NH}_3]^2/[\mathrm{Ag}(\mathrm{NH}_3)_2^{\cdot}] = K_{\mathrm{instability}} = 7{\cdot}41 \times 10^{-8}\,{}^{\ddagger} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad \text{(iii)}$$

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[*] Derived by interpolation from the collected data in Mellor's "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. 3.

[†] Mean of values derived from data of Kohlrausch and Dolezalek (*Berlin Akad. Ber.*, 1901, 101), Böttger (*Z. physikal. Chem.*, 1903, **46**, 602; 1906, **56**, 93), Abati (*Gazzetta*, 1906, **36**, ii, 834), Prud'homme (*J. Chim. physique*, 1911, **9**, 519), Kolthoff (*Z. anorg. Chem.*, 1921, **119**, 202). Solubilities for 15° were calculated from the available data, using Thomsen's value of 20·1 Cals. for the heat of solution of AgBr. Individual values ranged from 3·12 to 5·34 × $10^{-7}M$.

[‡] Britton and Wilson, J., 1933, 1050.

Assuming $[NH_3]$ to be large in comparison with the total dissolved silver, it follows that for the halide AgX

$$[X'] \approx [NH_3]^2 S_p/7{\cdot}4 \times 10^{-8}\ [\text{Total Ag}] \quad . \quad . \quad . \quad . \quad . \quad (iv)$$

If the only source of silver is a single pure halide, then S_m, the molar solubility of this in ammonia,

$$= [X'] = [\text{Total Ag}] = [NH_3]\sqrt{S_p/7{\cdot}4 \times 10^{-8}} \quad . \quad . \quad . \quad . \quad (v)$$

An attempt is often made to control the ammonia concentration by using a freshly prepared, cold, saturated solution of ammonium hydrogen carbonate as the solvent. Such a concentrated solution always loses an appreciable but variable amount of carbon dioxide; the concentration of free ammonia produced by hydrolysis is therefore variable but will be of the order of $0{\cdot}1N$. If, before extraction, the silver halide precipitate is washed free from excess of soluble silver salt, the concentrations of chlorion and of total dissolved silver will be equal and of the order of $0{\cdot}005N$. If the preliminary washing of the precipitate is omitted, it is evident that the additional silver may be large in comparison with that which would be dissolved from the pure halide. Consequently, it may happen that in a series of experiments with the same precipitate of mixed halides, the silver dissolved varies from the minimum to 5 times that value. Equation (iv) shows that a five-fold variation in the total silver concentration, coupled with a two-fold variation in the ammonia concentration, gives rise to the possibility of a twenty-fold variation in the amount of halide dissolved.

If, to avoid this variation, the precipitates are thoroughly washed, another difficulty is encountered. From equation (v) it follows that

$$S_{m,AgCl}/S_{m,AgBr} = \sqrt{S_{p,AgCl}/S_{p,AgBr}} = 22 \quad . \quad . \quad . \quad . \quad . \quad (vi)$$

This ratio is undesirably small. If saturated ammonium hydrogen carbonate is used as an extractant, pure silver bromide will dissolve to the extent of $1{\cdot}5 \times 10^{-4}M$, and a marked turbidity will result on acidification. If the so-called carbonate ($NH_4HCO_3,NH_2{\cdot}CO{\cdot}ONH_4$) were used, this turbidity would be still greater. By sufficiently reducing the ammonia concentration of the extracting reagent, the bromide dissolved may be diminished to an amount arbitrarily considered to be negligible, but since the maximum chlorion concentration is limited to 22 times that of the bromion, even a large proportion of chloride in the substance examined can only give rise to a slight turbidity. Consequently, it is impossible to form a satisfactory judgment as to the quantity present. Moreover, the visibility of turbidity depends on the conditions of illumination, and hence even in this modification of the test a slight turbidity must be discounted.

The efficacy of an ammoniacal reagent for dissolving silver chloride from the mixed halides is still further reduced, first, because of adsorption losses, and secondly, because of the time necessary for the dissolution of the maximum quantity of chloride.

Principles Underlying the New Method.—A consideration of equations (iv) and (v) shows that the ratio of the solubilities of silver chloride and bromide can be increased from 22 : 1 [equation (vi)] to approximately the square of this (500 : 1), by first washing the mixed halide precipitate free from a fortuitous excess of silver nitrate, and then adding a suitable measured excess of this reagent. The difficulty of achieving complete extraction is overcome by dissolving the entire precipitate in concentrated aqueous ammonia, and adsorption losses are reduced to a minimum by slowly precipitating the silver bromide by boiling off the excess of solvent. After filtration, an acid is added which contains sufficient mercuric nitrate to prevent the turbidity which would otherwise be produced by a pure bromide, the effect being due to the formation of $HgBr_3'$ and possibly other complex ions. This method of avoiding a precipitate due to bromide not only facilitates the detection of traces, but enables the ammonia to be used in sufficient concentration to dissolve a relatively large amount of silver chloride. This procedure makes it especially necessary that a definite final concentration of ammonia should be easily reproducible, since the solubility of the halide is proportional to the square of the ammonia concentration and not to the first power as would be the case if no excess of silver nitrate were added [see equations

(iv) and (v)]. The method described below, in which regular additions of ammonia are made during the boiling, gives satisfactory results when the chlorion is present to the extent of not less than 0·5% of the bromion.

In order to adapt the test to the detection of minute traces of chloride it seemed desirable to devise a suitable buffer with respect to ammonia. At first it was hoped that ammonium carbonate or hydrogen carbonate would serve, but consideration of the equilibria involved showed that the buffering effect would be slight. From the equation defining K_b it can be shown that

$$\frac{[NH_4OH]}{[NH_4^{\cdot}] + [NH_4OH]} = \frac{K_w}{K_w + K_b[H^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(vii)}$$

From this it will be clear, first, that since one effect of adding ammonia is to decrease the hydrogen-ion concentration, the ratio of free ammonia to total ammonium compounds will increase, and this can be almost entirely prevented by a sufficiently good hydrogen-ion buffer. Secondly, if a solution perfectly buffered with respect to p_H, in which [total NH_4] = $n[NH_4OH]$, be compared with a solution containing only ammonium hydroxide of the same concentration, it will be seen that a small addition of ammonium hydroxide to the former will cause a relative increase of [total NH_4], and consequently of $[NH_4OH]$, amounting only to $1/n$ of the corresponding increase in the unbuffered solution. Now, in the case of carbonic acid partially neutralised by ammonia, the hydrogen-ion buffer action is good only for p_H values in the region of 6—7. Such a mixture, which contains far more carbonic acid than corresponds to the hydrogen carbonate, would be of no practical value partly because of its instability, and partly because $1/n$ is so small (*ca.* 10^{-3}) that no practicable concentration of ammonium salts would give an adequate concentration of free ammonia.

A consideration of the practical requirements shows that an efficient buffer in the region of p_H 8 is required, and hence it is necessary to use either a weak acid of K_a *ca.* 10^{-8}, or a mixture of an ammonium salt with a partially neutralised weak base of K_b *ca.* 10^{-6}. It is essential that the reagent should not readily reduce silver compounds, and desirable that it should be capable of forming a highly concentrated solution. The only acid which seemed suitable was veronal, but its solubility was found to be undesirably low even when alcohol, acetone, or methyl ethyl ketone was used in the preparation of the buffer solution. The use of nicotine seemed promising since K_b for the pyrrolidine nitrogen is $4{\cdot}90 \times 10^{-7}$ (Lowry and Lloyd, J., 1932, 1626). Preliminary experiments on the solubility of silver chloride in solutions containing nicotine (a full discussion of which will be published later) can best be interpreted on the assumption that a complex $Ag(C_{10}H_{14}N_2)_2^{\cdot}$ is formed, having an instability constant of about 6×10^{-6}. On these assumptions it can be shown that the molar solubility of a silver halide

$$S = \frac{4170\ S_p}{c}\left[b_1^2\left(\frac{b + b_1 - a}{a - b_1}\right)^2 + 4(b + b_1 - a)^2\right] \quad . \quad . \quad . \quad \text{(viii)}$$

where a, b, b_1, and c represent respectively the normalities of strong acid radical, total nicotine, ammonia, and total silver in the solution. The dependence of the solubility on the presence of ammonia and nicotine respectively is indicated by the first and the second term within the square bracket. It will be evident that the change in the value of the first term for a small change in the value of b_1 is very much greater than the corresponding change in the algebraic part of the second term, which may be made relatively small if b_1 is small in comparison with $(b—a)$. Hence, provided the solubility due to nicotine can be made large enough for the practical requirements of the test, it will be advantageous to choose concentrations such that when the buffer is mixed with the test solution, the concentration of free ammonia will be reduced to negligible proportions, the final solubility of silver chloride being due almost entirely to the nicotine. This is feasible if a bromide is to be examined for chloride present to the extent of 1% or less.

The adequacy of the buffer was checked experimentally by carrying out blank tests using the procedure of Method II (p. 788), but with the addition of an abnormally large quantity of ammonia solution towards the conclusion of the boiling, and comparing the turbidities finally obtained with those which resulted when the blank test was carried out normally. It was found that a 1200% increase in the ammonia concentration only increased the turbidity due to bromide by 20—30%. The maximum observed variation in the final ammonia concentration due to accidental variations in the procedure amounted only to 300%. It may be concluded, therefore, that the nicotine buffer is entirely satisfactory for use in the test described.

EXPERIMENTAL.

Examination of Method based on Extraction by Ammonium Hydrogen Carbonate.—Preliminary experiments, in which no special precautions were taken to control the variable factors discussed above, showed that the turbidities finally obtained on testing a pure bromide were very variable and frequently greater than those which resulted on testing a bromide containing 3 equivs. % of chloride.

Quantitative experiments were then carried out in which the silver halide precipitate was washed free from excess of silver nitrate, and *M*-ammonium hydrogen carbonate was used instead of the more variable saturated reagent; moreover, mercuric nitrate was employed to prevent the formation of a precipitate in the case of pure bromide. The results shown in Table I were obtained by adding an excess of silver nitrate to a series of solutions containing 1·4 c.c. of *N*-ammonium bromide and varying amounts of sodium chloride. The resulting precipitates were washed, extracted with 70 c.c. of *M*-ammonium hydrogen carbonate, and 25 c.c. of the resulting solution were treated with 5 c.c. of either 6*N*-nitric acid or $5{\cdot}4 \times 10^{-4}M$-mercuric nitrate in 6*N*-nitric acid. A comparison of the results obtained with and without the use of a mercuric salt shows that the amount of this reagent necessary to suppress the precipitate that would otherwise result from a pure bromide also retains in solution about 0·6 mg. of silver chloride per 30 c.c. The maximum amount of final silver chloride precipitate which can be obtained is, even in the case of a pure chloride, only 17 times the minimum amount which must be exceeded if any indication of chloride is to be obtained. The effect of this small solubility of silver chloride in limiting the maximum possible percentage yield is shown in the last line in Table I. Comparison of these limiting values with the yields actually obtained shows that the extraction is very inefficient even after 5 hours' standing. If the extraction is short, the test is grossly lacking in sensitiveness, and even positive results are no safe guide as to the proportion of chloride present; *e.g.*, the weight of precipitate from the 23% mixture was much less than that from the 10% mixture.

TABLE I.

Results obtained by extraction with ammonium hydrogen carbonate.

Duration of extraction, hrs.	Hg concn. in final soln., $M \times 10^{-5}$.	Equivs. Cl′ per 100 equivs. Br′ + Cl′.				
		1.	3.	10.	23.	100.
		Wt. of final ppt., mg.				
$\frac{1}{4}$	9	nil	nil	0·88	0·43	—
5	9	nil	0·55	1·47	—	10·3
5	—	0·54	1·1	2·1	—	11·0
		Yield of final precipitate, %.				
$\frac{1}{4}$	9	nil	nil	12	2	—
5	9	nil	26	20	—	8·7
		Solubility limit to percentage yield.				
		100	100	87	29	8·7

Precipitation of Silver Bromide from a Solution of Silver Chloride and Bromide in Ammonia.—Since the above experiments show that extraction of silver chloride by weakly ammoniacal solutions was very imperfect, it seemed essential to dissolve the entire precipitate in concentrated ammonia; slow reduction in the ammonia concentration might then be expected to precipitate nearly all the bromide, the conditions ensuring minimum loss of chloride by adsorption. Preliminary attempts involving the passage of carbon dioxide or the dropwise addition of an acid, showed that reproducible results could not be obtained with the aid of acid–alkali indicators. Boiling for a specified time was also unsatisfactory, but it was ultimately found that if during the boiling the loss of liquid were roughly made good, approximately once a minute, by the addition of ammonia, a state was soon reached which was to a large extent independent of the rate of boiling. The following table shows the final concentrations of ammonia obtained under various conditions.

Vol. made up each minute to	Concn. of added NH_4OH.	No. of observations.	Final concentrations of NH_4OH, *N*. Limits.	Median value.	Arithmetic mean.
50 c.c.	6*N*	22	0·142—0·350	0·24	0·24
50 c.c.	3*N*	15	0·125—0·218	0·15	0·16
50 c.c.	2*N*	11	0·095—0·186	0·13	0·14
40 c.c.	3*N*	16	0·052—0·160	0·090	0·093
20 c.c.	3*N*	21	0·016—0·055	0·031	0·032

It will be evident that the volume chosen is of great importance since it has a marked effect, not only on the final ammonia concentration, but also on the variability of this concentration, due to unavoidable variations in procedure; a volume of 50 c.c. shows relatively less variation between maximum and minimum than one of 20 c.c. In all cases the median value closely corresponds with the arithmetic mean, and the distribution between the limits is practically symmetrical; but with the smaller volumes the upper limit was less well-defined than the lower one. The necessity of using such a concentration of mercuric salt as will suffice when the ammonia concentration is a maximum, necessarily makes the test less sensitive than would otherwise be the case. It has, however, been found that for the recommended procedures the maximum amount of silver chloride which can be dissolved is about 100 times the minimum detectable amount.

The Use of Excess of Silver Nitrate.—Preliminary attempts to carry out the separation with the aid of a nicotine buffer, but without excess of silver nitrate, gave much smaller turbidities than were anticipated from the solubilities of silver halides in nicotine, and the capacity of the test to discriminate between bromide and chloride was surprisingly poor. This was found to be due to the fact that the total molar concentration of silver in the solution, after boiling off excess of ammonia, was considerably less than the sum of the halide concentrations, especially when the final ammonia concentration was very low. Nephelometric tests on solutions resulting from the treatment of a pure bromide gave the following results :

Final $[NH_4OH]$.	$[\mathrm{OH}'] \times 10^4$.	$[\mathrm{Br}'] \times 10^4$.*	$[\text{Total Ag}] \times 10^4$.*	$[\mathrm{Br}']/[\text{Total Ag}]$.
0·006	3·5	1·1	0·037	30
0·008	4·0	1·2	0·06	20
0·012	4·9	1·6	0·11	14
0·02	6·3	2·1	0·23	9
0·13	16	4·4	4·4	1

* These results were taken from a smoothed curve, individual determinations being liable to vary from them to the extent of 15%.

The solubility product of silver hydroxide would only be exceeded if $[\mathrm{OH}'] > 10^5 [\mathrm{Br}']$, and it will be seen from the above data that this condition is not approached. In view of the preferential adsorption of silver ions by a silver halide sol, it seems likely that on flocculation hydroxyl ions will be adsorbed, especially as their concentration exceeds that of the bromide ions. Such adsorption effects provide a further reason, in addition to that discussed on p. **784**, for the use of an excess of silver nitrate. This not only secures a definite and relatively high concentration of total silver in solution, but by reducing the solubility of both halides it permits the use of a higher ammonia concentration, and thus minimises the adsorption effect in question, as will be seen from the above table.

The addition of silver nitrate must precede the final acidification, since the deficit of silver at the time of filtration will already have caused the bromion concentration to be abnormally high, without increasing the chlorion concentration, for, under the working conditions, practically the whole of the chloride present will in any case go into solution. It remains to be considered whether the addition should be made before or after the boiling. In the former case the solubility of silver halides will be reduced in the ammoniacal solution as well as in the final buffer mixture, and consequently the boiling must be conducted so as to leave a higher concentration of residual ammonia than would be necessary in the second case. This would constitute a disadvantage if it caused the halide solubility due to ammonia in the final buffer mixture to approach the solubility due to nicotine. Insertion of practically useful concentrations in equation (viii) shows that the effect is negligible for most purposes. Experiments showed that there is little to choose between the alternatives. The higher ammonia concentration required when the silver nitrate is added at the outset is best obtained by using a larger volume of solution for the boiling. Since the alternative method more conveniently permits of considerable concentration during the boiling, it is to be preferred for the detection of very minute traces.

Procedure.

Reagents.—A.R. Reagents are satisfactory for the general form of the test, but the ammonia should be tested for freedom from chloride. Some A.R. reagents (*e.g.*, sodium carbonate) are liable to contain slight traces of chloride, but the mercuric nitrate concentration recommended is sufficient to prevent interference.

For the detection of traces of chloride, a *chloride-free bromide* is essential for the blank test. A.R. Potassium bromide generally contains 0·3—0·7% of chloride, but approx. *N*-ammonium bromide can be prepared from A.R. bromine (freed from chlorine by washing with aqueous sodium hydroxide; Scott, J., 1913, **103**, 850) by placing 5 c.c. of it under water, adding *ca.* 50 c.c. of 6*N*-ammonia (with cooling and shaking), boiling off excess ammonia, and diluting to 200 c.c.

Nicotine. Commercial 95% nicotine was distilled in a current of nitrogen, and colourless material of b. p. 160—180°/25 mm. was carefully bottled; this was suitable for the test even after 3 months. *Nicotine buffer.* Concentrated sulphuric acid (3 c.c.) is mixed with about 30 c.c. of water, cooled, added to 40 c.c. of nicotine, and diluted to 80 c.c.

Method I (*without Buffer*), *Suitable for Detection of Chloride not Less than* 0·2% (*by Wt.*) *of Bromide.*—If necessary, remove cyanides and other interfering radicals by the usual methods. To a portion of the solution containing not more than 40 mg. of bromion, add dilute nitric acid until the acidity is about *N*, followed by a small excess of silver nitrate. Wash the precipitate three times by decantation, dissolve it by shaking in a stoppered vessel with 50 c.c. of 6*N*-ammonia, add 5 c.c. of 0·1*N*-silver nitrate, and transfer to a 150 c.c. beaker (tall pattern) previously marked on the outside at the 50 c.c. level. Boil the solution vigorously for 3 minutes (see Note 1), and make the volume up to 50 c.c. by addition of 3*N*-ammonia, without interrupting the heating. Continue to make up the volume at intervals of about one minute until four additions have been made. Boil for one minute longer, cool, and filter. Mix the filtrate with one-fifth its volume of $4 \times 10^{-3}M$-mercuric nitrate in 6*N*-nitric acid. A turbidity or precipitate indicates the presence of chloride.

Note 1. The use of an anti-bumping rod is recommended during the boiling (Scudder, *J. Amer. Chem. Soc.*, 1903, **25**, 163); the tubes used were of 3 mm. internal diameter.

Note 2. If a sintered-glass filter (Jena No. 4) is used, filtration may be carried out immediately after cooling; but if filter-paper is used, it should be fine, and the turbid liquid should be slightly cooled, transferred to a stoppered vessel, and shaken vigorously from time to time whilst cooling to the ordinary temperature.

Method II (*with Nicotine Buffer*), *Suitable for Detection of Very Slight Traces of Chloride.*—Make and wash three times as much of the mixture of silver halides as was recommended for Method I (see Note 1). Simultaneously carry out a blank test by precipitating silver bromide from 3 c.c. of chloride-free *N*-ammonium bromide. In each case dissolve the precipitate by shaking in a stoppered vessel with 40 c.c. of concentrated ammonia (*d* 0·880), and evaporate the solution to half bulk in a basin on a steam-bath. Decant the liquid from the precipitated silver bromide into a tall-pattern 150 c.c. beaker previously marked at the 20 c.c. level. If the volume is less than 20 c.c. make it up with 3*N*-ammonia. Boil vigorously, making up the volume at intervals of a minute until four additions have been made. Boil for 1 minute after the last addition, cool to about 50°, add 8 c.c. of the turbid solution to 4 c.c. of nicotine buffer, and add the mixture to 0·5 c.c. of 0·1*N*-silver nitrate and set aside in the dark for at least ½ hour (see Note 2). Filter, and to the filtrate add one-fifth of its volume of 8—12*N*-sulphuric acid. The presence of chloride is indicated if after 5—10 minutes' standing the turbidity in the test solution is appreciably greater than in the blank as viewed in ordinary light. If the solutions are compared in a nephelometer, a difference of 40% should be ignored, but any larger difference may be regarded as certain evidence of the presence of chloride. In the absence of a nephelometer, a Walpole type of comparator may be used for qualitative purposes, the solutions being observed by looking down the tubes which are illuminated horizontally.

Note 1. Under the conditions recommended, the buffer limits the chloride solubility to that present in a mixture containing 0·25 mg. Cl per 100 mg. Br. If it be desired to extend the range of the test, *e.g.*, to cover the range of chloride liable to be present in A.R. bromide, only one-third as much of the original substance as recommended above should be taken. The sensitivity will then be 0·006 mg. Cl per 100 mg. Br.

Note 2. Although the extra precipitate which is formed when the mixture is added to the silver nitrate comes out in a very finely divided form, it should be possible to obtain a perfectly clear filtrate after ½ hour's standing if a fine-pored filter is used. Mixing the solutions while still hot helps to ensure this. The filtrate should be acidified without undue delay, since on prolonged standing a further turbidity may arise. Provided the test solution and the blank be treated in the same way, the comparison may be effected after ½ hour's standing. If, however, extremely slight traces are sought, rather longer standing is desirable (preferably overnight), as the turbidity of the blank will then be somewhat less.

Note 3. The use of a mercuric salt is not recommended when testing for very slight traces of chloride. In such a case it is essential to carry out a blank test with the reagents, and the turbidity due to bromide in this form of the separation is very slight.

Note 4. Attention is called to the fact that a dangerously poisonous amount of nicotine can readily be absorbed through the skin. It should at once be washed off with *cold* water.

TABLE II.

Yields % obtained by Method I.

Total halide taken = 0·5 c.c. of *N*-solution; 5 c.c. of 0·1*N*-$AgNO_3$ added before boiling; volume made up each minute to 50 c.c.; volume after boiling = 45—47 c.c.

Concn. of added NH_4OH.	Equivs. Cl′ per 100 equivs. Br′ + Cl′.							
	0·3.	0·5.	1.	3.	10.	30.	50.	100.
6*N*	? t. (3b)	v.s.t. (10b)	84	89	87	84	100 (46—100)	72 (26—100)
3*N*	v.s.t. (10b)	s.t. (18b)	m.t.	81	88	92	80 (36—100)	49 (20—62)
2*N*	v.s.t.	s.t. (32b)	m.t.	81		85	43 (21—80)	24 (12—45)

Turbidities: v.s.t. = very slight turbidity; m.t. = marked turbidity; 3b = turbidity 3 times that obtained in blank test, and so on. Sufficient $Hg(NO_3)_2$ was used in all series to ensure that the blank appeared clear under ordinary conditions of illumination. The minimum turbidity easily detectable without a nephelometer was about 10b.

Yields (determined gravimetrically). In the last two columns yields corresponding to the mean value for NH_4OH are first given, followed in parentheses by the limits. These yields were calculated from the experimental data on the assumption, justified by the results, that the yield when limited by the ammonia concentration is proportional to $[NH_4OH]^2$. Yields given in other columns are the direct results of single experiments or the arithmetic means of several, and are not materially affected by small variations in the ammonia concentration.

TABLE III.

Turbidities obtained by Method II.

Method II A: $AgNO_3$ is added after boiling off excess of NH_4OH. Total halide taken = 3 c.c. of *N*-solution. During boiling, volume made up each minute to 20 c.c.

Method II B: $AgNO_3$ (2 c.c. of *N*/10) added before boiling off excess of NH_4OH. Total halide taken = 3 c.c. of *N*-solution. During boiling, volume made up each minute to 40 c.c.

	Equivs. Cl′ per 100 equivs. of Br′ + Cl′.								
Method.	0.	0·005.	0·01.	0·03.	0·06.	0·25.	0·5.	1.	3.
II A	1	1·6	2·1	4·1	—	—	64	80	—
II B	1	1·5	2·1	3·8	6	25	60	—	350

Discussion of Results.—Particulars of the results obtained are given in Tables II and III. It will be seen that if the concentration of the added ammonia is increased to 6*N*, the percentage yields obtained are somewhat improved for cases where the proportion of chloride is high, but the final ammonia concentrations are more erratic and the test becomes somewhat less sensitive. On the other hand, if the concentration of added ammonia is reduced to 2*N*, the precipitate from a pure chloride is only of the same order of magnitude as that obtained when the chlorion concentration is 30% of the bromion concentration. The use of 3*N*-ammonia appears to be the best compromise, since, for mixtures containing up to 50 equivs. % of bromide, the yields are of the order 80—90%, and thus afford a fair criterion of quantity. Since the test in its simple form will readily permit the detection of chloride down to 0·5 equiv. % (*i.e.*, 0·2 mg. Cl′ per 100 mg. Br′), it will show the presence of amounts exceeding those permissible in A.R. material.

Method II will detect chlorion down to 0·002 mg. per 100 mg. of bromion, and the yields obtained are sufficiently regular to permit of nephelometric comparison with the turbidities produced from samples containing known percentages of chloride. This method is limited as to the maximum amount of chloride which can be dissolved (see Note 1), but if it were desired to prepare a buffer capable of dissolving a much larger quantity of silver chloride, this could readily be done by the addition of an ammonium salt to the buffer here recommended.

This investigation has shown that, although the ammonia separation in its original form is very inefficient, yet, with the modifications now described, it is capable of giving results which are adequate for all qualitative purposes and for the nephelometric estimation of very minute traces. In sensitivity, the nicotine method compares favourably with Noyes's permanganate method ("Qualitative Chemical Analysis," 1922, 9th Edn.) and Orlow's manganese dioxide method (*Z. anal. Chem.*, 1931, **84**, 185). It is intended shortly to describe comparative tests carried out with these and a number of varieties of differential oxidation methods. The minimum amount detectable by the nicotine method could scarcely be found by those quantitative methods which virtually amount to the determination of the equivalent of bromine, since this would be affected by only 0·003% of its value.

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