the interference of the precipitates with the end-point is negligible.[1] Dynamic theory is thus throughout in agreement with the verdict of our experiments.

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ON THE DIRECT QUANTITATIVE SEPARATION OF CHLORIDES AND BROMIDES

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Introduction.

The direct separation of chlorine from bromine has always been considered one of the most difficult problems of quantitative analysis, excepting those relating to the rare earths and the radioactive elements. The standard works on quantitative analysis usually content themselves with a discussion of indirect methods, omitting any description of processes for direct separation.

Practically all the methods recommended for the direct separation of these elements rest on oxidation reactions applied to solutions of bromides and chlorides. The difference between the oxidation-potential of a solution of chlorine in potassium chloride and water, and that of a corresponding solution of bromine is about 0.241 volt.[2] Numerous oxidizing agents have been employed, always in acid solution, that is in the presence of solutions more or less concentrated as regards hydrogen ions. In every case investigated, excepting one, the oxidant used possesses a higher oxidizing potential than that of an aqueous solution of chlorine. Hence in such cases, the success of the operation must depend on interrupting the process exactly at the point when all bromine is liberated, since if prolonged beyond that point, some chlorine would also be set free. Methods subject to conditions of this sort can not be looked upon

[1] Taking Böttger's (loc. cit.) figures for the solubilities of AgBr and AgCNS and Kohlrausch and Dolezalek's figure (Ber. Berlin. Akad., 1901, p. 101) for the solubility of AgI, the ratios of the solubility-products involved are as follows:

$$\frac{S^2_{AgBr}}{S^2_{AgCNS}} = \frac{C^-_{Br}}{C^-_{CNS}} = \frac{2.03 \cdot 10^{1-3}}{6.84 \cdot 10^{-13}} = \text{about } 0.3,$$

(that is, of a drop of sulphocyanate added, 3/13 will be changed to bromide, but 10/13 will remain unchanged);

$$\frac{S^2_{AgI}}{S^2_{AgCNS}} = \frac{C^-_{I}}{C^-_{CNS}} = \frac{2.25 \cdot 10^{-16}}{6.84 \cdot 10^{-13}} = \text{about } 0.00033$$

(that is, of a drop of sulphocyanate added, only about 1/3000 will be changed to iodide).

[2] Bancroft, Z. phys. Chem. 10, 405 (1892).

as other than empirical. They can give results approximating the truth, only by a minute regard to all the circumstances of the reaction, as temperature, degree of acidity, concentration, etc., and only then by a happy compensation of errors.

Bugarszky[1] first pointed out the necessity of selecting as an oxidant, one, of which the oxidizing potential should be intermediate between that of chlorine and that of bromine. With this principle in view, he made use of iodic acid as an oxidizing agent. It has an oxidation potential 0.064 volt higher, according to Bancroft than that of an equivalent and equally acidified bromine solution. A very careful examination of Bugarszky's method, in comparison with a considerable number of other methods, has confirmed that investigator's observations in most essential respects and has convinced me that his is by far the best method yet published. It is true that the process of Engel[2] is capable of giving reasonably exact results, especially with certain modifications of which the most important is the exclusion of ammonium salts. The feature of the latter method is the use of a perdisulphate as oxidant. Engel employed the ammonium salt, $(NH_4)_2S_2O_8$. The method has serious drawbacks. One of these is the oxidation of part of the bromide and chloride to bromate and chlorate, which takes place under conditions not easily defined but seemingly due to small amounts of catalyzing agents. Since the chlorate and bromate must be afterward .reduced and the whole process repeated in order to complete the desired separation, I felt compelled to abandon the method after a good deal of experience with it.

Briefly stated, Bugarszky's method consists in adding to the bromide-chloride solution, sulphuric acid and potassium di-iodate, then distilling. The bromine and iodine liberated in accordance with the equation

$$KH(IO_3)_2 + 10\ KBr + 11\ H_2SO_4 = 11\ K_2SO_4 + 10\ Br + 2\ I + 6\ H_2O$$

pass off with the steam. The remaining solution contains the hydrochloric acid and the excess of iodic acid. Bugarszky observed that when the bromine was determined by absorbtion of the vapor in potassium iodide and subsequent titration of the iodine, the amount of bromine found was considerably less than that taken, in consequence of a portion having been reduced by the steam to hydrobromic acid with liberation of oxygen. He therefore recommends determining the bromine by titration of the unconsumed excess of iodate remaining in the mother liquor. He overlooks, strangely enough, the fact that if the first named procedure gives too low figures for the bromine ; the second must lead to results that are too high, because, a part of the bromine being reduced to hydrobromic acid in the solution and in the condensed and returned

[1] Z. anorg. Chem. 10, 387 (1895).

[2] Engel C. R. 118, 1263 (1894).

steam, it must be again oxidized at the cost of the iodic acid.   This obvious reasoning is fully confirmed by my experiments, which showed always results too high by titration of the iodate excess (by 1.0 to 1.5 per cent.)   Hence the determination of the bromine should be made by the alternative method of Bugarszky, viz., absorbtion of the vapor, containing steam, bromine and hydrobromic acid, in a reducing solution, with following titration of the bromide according to Mohr or Volhard, or gravimetric estimation.

As regards the determination of the chloride in the mother liquors, I was able to get results of the same accuracy as the test analyses of Bugarszky.   These results are satisfactory when the relative amount of chlorine is large, but were not sufficiently so for my purpose when the chlorine percentage is low.   The causes of inaccuracy in this case do not lie in any imperfection of the main reaction but are as follows.

(1) The maximum amount of substance taken by Bugarszky is 0.400 gram.   This can not well be exceeded without other modifications of the method.

(2) The presence of considerable quantities of sulphuric acid and sulphates interferes noticably with the precision of the Volhard method when the amount of chloride is very small, because appreciable amounts of difficultly soluble silver sulphate are dragged down with the chloride and sulphocyanate.

(3) Bugarszky gets rid of the iodic acid before determining the chlorine by first reducing to iodide with sulphurous acid, then expelling the iodine by boiling with sodium nitrite.   This procedure is open to objection.   It is no easy matter to prepare or to buy sodium nitrite free from chloride.[1]   If any trace of nitrous acid is left in the solution it will, as is well known, interfere with the sharpness of the end-reaction in the Volhard titration.   Further, the process leaves a considerable additional amount of foreign salts in solution and especially of sulphate, disadvantageous for reasons stated under (2).   As a matter of fact it is not necessary to remove the excess of iodic acid at all.   If the solution is sufficiently diluted and acidified with nitric acid iodic acid only interferes in a minor degree with the titration, the error being of about the same order as that introduced by the presence of sulphates; negligible therefore except when the amount of chloride is small.

To increase the accuracy of the method it accordingly seemed advisable, to increase the amount of substance taken, to replace the sulphuric acid by nitric acid, to remove the excess of iodic acid by a single reagent which would introduce no sulphate or other injurious compound and the

[1] It is to be remembered that silver chloride is to a considerable extent soluble in solutions of sodium nitrite, hence, the salt must be wholly decomposed before testing for chloride.

excess of which would require no removal. It would take too much space to recount the steps by which these objects were attained and several additional advantages incidentally gained. Before presenting details of the procedure finally adopted it will suffice to say that the removal of the iodic acid is best effected by the use of phosphorous acid. This substance possesses almost ideal properties for the purpose. Under the conditions, it reduces iodic acid to free iodine, quantitatively, not leaving even the slightest traces of iodide in the solution. The iodine can be readily boiled off and the excess of phosphorous acid does not in the least interfere with any subsequent operations. Experience has demonstrated that in expelling the bromine it is not sufficient to distil till the solution is colorless as prescribed by Bugarszky, since at this point traces of bromine may still remain, as shown by fluorescein paper (Baubigny) or by the still more sensitive tests mentioned below. It proved to be desirable to use an amount of bromide for the analysis, increasing as the amount of chloride diminishes, and an amount of iodate such that the excess of iodic acid shall be approximately constant. A similar consideration is valid for the nitric acid. The effect of this adjustment is, that when the amount of bromine to be expelled is larger the solution is more acid at the beginning, but the final acidity at the close of the reaction is approximately the same. Hence, it does not take much longer to expell the larger amounts of bromine than the smaller, the reaction being slow only when nearly complete.

For the determination of chloride in crude potassium bromide, the following table will serve as a guide to the amounts of substance and reagent to take. In case of other bromides quantities equivalent to those given should be used.

If the KBr-KCl has % of KCl	Weight of KBr + KCl	Fifth-normal Iodate KIO$_3$	Nitric Acid, Approximately Double Normal.
5 to 10	0.6 gram	36 cc.	20 cc.
1.5 to 5	1.8 gram	96 cc.	26 cc.
0.25 to 1.5	3.6 gram	186 cc.	35 cc.

The Analysis.

Select a Kjeldahl flask of 400 to 500 cc. capacity and having a neck 20 to 25 cm. long. Introduce into it the chloride-bromide mixture, add the potassium iodate solution and the nitric acid and enough water to bring the volume to 200 or 250 cc. Support the flask at an angle of about 30° from the vertical, resting on a hole about 2½ inches in diameter, in a square of heavy asbestos board. The latter is of course intended to deflect the hot flame gases from the sides of the flask. The neck acts as a reflux condenser returning to the flask traces of hydrochloric acid which might otherwise escape when the volume of the liquid

is reduced to its minimum. Heat to gentle boiling with a bunsen flame. It is advantageous, but not by any means necessary to begin this opera-tion near the close of a day's work and after boiling for five minutes to allow the solution to stand over night. The reaction goes on while standing and thus shortens the actual period of boiling. In any case, boil down to a volume of about 90 cc. This point should be permanently marked on the outside of the flask in such a way as to correspond to its slope. When the amount of chloride is small, the volume may be reduced to 60 cc. without measurable loss, but in general the 90 cc. mark should not be passed. The boiling ought to go on at such a rate that 30 to 40 minutes are required. The solution is now usually per-fectly colorless and only traces of bromine remain. Add 100 cc. of water and continue the boiling until 50 cc. have passed off. The escaping vapor may now be tested with fluorescein paper, held across the mouth of the flask for five minutes. If no change of color from yellow to orange occurs, the final test may be made. For this purpose, pass the escaping steam, with the help of a clean rubber stopper and narrow bent glass tube through ten cubic centimeters of a 2 per cent. solution of potassium iodide to which enough decinormal hydrochloric acid has just been added to impart a faint acid reaction, in a test tube ; until the solution has become hot (about 40 seconds). If this liquid shows no yellow color when held against a white surface the bromine may be regarded as expelled.[1] This test is more delicate than fluorescein or than sodium bicarbonate solution faintly tinted with indigo.

When the bromine is all expelled, add, without interrupting the boil-ing, 1.0 to 1.50 cc. of a twenty five per cent. solution of phosphorous acid. Continue the boiling till all iodine is driven off, as shown by the color, and five minutes longer. This requires about ten minutes in all. At no time may the volume be allowed to become less than 90 cc. (except in the case previously mentioned when the total amount of chlorine is small, a few milligrams).

To the water-white and cooled solution in the flask add a moderate excess of twentieth or of fiftieth normal silver nitrate solution (accord-ing to the amount of chloride present) then a fragment of the best filter paper and shake violently till the paper is reduced to pulp. Filter, wash, add 5 cc. of ten per cent. ferric nitrate solution and titrate after Volhard with twentieth or fiftieth normal sulphocyanate till colored and then back with the silver solution. The endpoint can always be more exactly hit in this direction.

The freedom from chlorine of all reagents should be controlled. The

[1] It is hardly necessary to say that the iodide must be pure and able to stand heating under the conditions prescribed, without any coloration, when bromine is absent.

standard potassium or ammonium sulphocyanate will not give a sharp end reaction, if it contains chloride. It may be tested in the same way as a bromide, i. e. decomposing by boiling with nitric and iodic acids, etc.

The fifth normal potassium iodate solution contains 7.138 grams. of the purest recrystallized salt to the liter. If preferred, a normal solution may, of course be employed instead.

The freedom of this salt and of the other reagents from chlorine may best be determined by a blank analysis on 2 grams of the potassium iodide, using the regular amounts of iodate, nitric acid and phosphorous acid. Phosphorous acid is the only reagent which can not easily be found free of chlorine, and the amount used is so small that a trace of chlorine in it does not as a rule matter much, as the error so introduced is usually less than 0.01 per cent.

The following analyses of mixtures of known composition will serve to show the degree of accuracy to be expected from the method. A nearly pure potassium bromide, containing 0.025 per cent. of chloride was mixed with varying amounts of potassium chloride and the mixture then analyzed by the method described. The first column gives the weight in grams of the bromide taken ; the second, the weight of potassium chloride added (in the form of a standard solution) ; the third, the total amount of chloride present ; the fourth, the number of cubic centimeters of standard silver solution consumed ; the fifth, the weight of potassium chloride found ; the sixth, the percentage of chloride actually present ; the seventh, the percentage of chloride found.

Bromide taken	Chloride added	Total chloride	Silver solution	Chloride found	% KCl present	% KCl found
			N/50			
3.6000 g	000	0.0009	0.60 cc.			0.025
3.6000	0.0361	0.0370	24.55	0.0366	1.077	1.06
3.6000	0.0722	0.0731	48.82	0.0728	1.991	1.982
			N/20			
3.6000	0.1083	0.1092	29.32	0.1094	2.945	2.950
3.6000	0.1444	0.1453	39.13	0.1459	3.880	3.896
1.8000	0.1444	0.1449	38.93	0.1452	7.453	7.467

Further, a mixture was made by me of pure potassium chloride and of a potassium bromide containing 0.07 per cent. of chloride, both pulverized, dried at 150° and then thoroughly incorporated in such proportion that the product contained 3.95 per cent. of chloride. Portions were then given to three chemists for analysis with no further information beyond the fact that the amount of chloride was between 1.5 and 5.0 per cent. Only one of these chemists had used the method before. They reported the following results :

Chemist "C" reported 3.93 per cent. of chlorine: "S" reported 3.98 and in a duplicate 3.88, with the remark that he thought this "too low,

since the evaporation has been carried much too far" ; "A", 4.02 ; "L", 3.96 per cent. There is no doubt that with practice even closer results than this set of analyses indicates can be regularly obtained.

Evidence of this is given by the analyses of crude bromine reported below.

The method has now been in constant use in this laboratory for six or eight months with uniformly satisfactory results.

Determination of Chlorine in Crude Bromine.

Crude bromine (of American origin) contains chlorine varying in amount from one to thirteen per cent or even more, a very minute amount of iodine, a small quantity of water (not far from 0.05 per cent), brominated organic matters derived from tallow, and small amounts of tar, formed by the action of bromine on coal tar. Some samples contain an easily recognizable quantity of bromoform, which is left as a nearly colorless liquid when twenty-five or fifty cubic centimeters of the bromine are allowed to evaporate in a current of air.

The percentage of chlorine may be determined by converting the sample quantitatively into a mixture of chloride and bromide by dissolving in caustic soda, evaporating to dryness, fusing in the presence of a little sugar charcoal, then analyzing the melt by the process already given for bromides.

A much shorter, more convenient and at the same time somewhat more accurate method consists in treating the weighed sample of crude bromine with a solution of an alkali iodide insufficient to react with all the bromine, but more than sufficient to retain all the chlorine in the sample. No chlorine escapes from this mixture on boiling, the amount of salt to be handled is less than would be the case if all the bromine were converted into bromide and, consequently a larger sample can be taken, which contributes materially to the accuracy when the percentage of chlorine is very low, for example, a few tenths or even thousandths per cent.

Before describing working details of this procedure, it is appropriate to draw attention to certain precautions necessary to observe in securing samples of the crude bromine for analysis and in handling them when obtained. Special precautions are imposed on account of the ease and rapidity with which the composition changes by evaporation of the chlorine. I have satisfied myself by actual analyses that it is impossible to pour bromine from one bottle to another, without a very appreciable diminution in chlorine percentage occurring. The ordinary temperature and an ordinary bromine of from 4 to 6 per cent of chlorine are here understood. A bottle containing about 600 grams, closed with a badly ground glass stopper stood in the laboratory about a month, during which

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period it was opened two or three times, just long enough to withdraw a
sample for analysis.   The chlorine gradually fell from 6.44 per cent to
5.58.   Another sample was allowed to stand in a narrow tall cylinder till
by evaporation its volume was reduced from 50cc to 39cc.   This resulted
in a diminution of chlorine from 6.2 to 3.4 per cent.

These facts are recorded in order to emphasize the propriety of drawing
samples by means of a suitable special pipette, without suction, from
beneath the bromine layer and of avoiding under all circumstances pour-
ing bromine to be analyzed from one receptacle to another.   When the
amount of chlorine exceeds two per cent, it is well to cool the bromine
bottle in ice water before taking the sample.

A suitable form of pipette for compositing samples can be made from an
ordinary 5cc. pipette by passing through the upper stem a glass rod which
at its lower end is ground to fit perfectly the lower opening of the bulb.
The lower stem is removed and replaced by a delivery nozzle only two or
three milimeters long, into which the ground joint extends so as to leave
no dead space.   In the centre or, as the case may be, in the upper part of
the bulb a hole about three or four milimeters in diameter is made.   In
use, the valve is lifted and the instrument is plunged quickly far below
the surface of the bromine.   The air escapes from the side opening, and
the filling is very rapid.   The pipette is now closed by depressing the rod,
and is raised above the liquid for a few seconds.   It thus drains on the
outside while inside the bottle.   It is now quickly lifted and permitted to
empty partially, or wholly, either into the chilled container used for com-
positing, or into the weighed glass-stoppered flask containing potassium
iodide solution.   For the latter purpose a pipette of similar construction
but smaller size is preferable.   The Lunge-Rey and other forms of
weighing pipettes have also been used for this purpose in this laboratory
with success.   Their disadvantage is that it has proved to be impossible
to get stop-cocks so perfectly ground on these instruments as to hinder
the escape of more or less bromine into the balance case. If used, graphite
is the only permissible lubricant.   It is impossible to entirely avoid loss
of chlorine during the manipulations, even with every precaution.   Since
this loss does not by any means increase in proportion to the weight of
bromine taken, it follows that a relatively large amount should be weighed
and the solution at a subsequent stage subdivided for analysis, if the
quantity of chlorine present is too large for direct titration.

The process.   Introduce about three grams of the bromine, accurately
weighed, or more if the chlorine content is below 0.5 per cent,
into a solution of two grams of potassium iodide in 50 cc. of
water contained in an Erlenmeyer flask with well ground stopper.   In
warm weather, flask and contents should be previously cooled in ice.
Quickly insert the stopper and shake. Transfer to a 400 cc. Kjeldahl flask,

disregarding the escape of vapors of iodine and bromine and, after rinsing, add 60 cc. of fifth normal potassium iodate (or 12 cc. of the normal solution), 24 cc. of nitric acid and water to make about 250 cc.   Proceed from this point precisely as in the analysis of a bromide (p. 278).   Of course, when the solution is ready for titration, an aliquot part should be taken, if the amount of chlorine is so large as to make this step desirable.

The bromine may for many practical purposes be determined sufficiently well by difference, since the total quantity of impurities other than chlorine is usually much less than one per cent.

If accuracy is desired, the total free bromine and chlorine should be determined by an iodometric titration, the weighed substance being dissolved in a considerable excess of potassium iodide solution, and the liberated iodine titrated after feeble acidification.   Correcting the volume of thiosulphate here required by that equivalent to the chlorine found, the difference gives the free bromine.

It is obvious that the accuracy of the method described for the determination of chlorine in bromine, or of any other process for this purpose, can not be shown by analyses of known mixtures, since the errors in preparing such a mixture must far exceed the analytical errors.   It is only possible to show the agreement of duplicate analyses and the concordance of the analytical results with physical properties.   The latter will be taken up in another paper.

As illustrative of the former, I take at random several analyses out of a large number, made by Dr. H. A. Carlton.

Sample 6706	Found % of Cl	2.445	2.380		
6806	" "	2.069	2.072	2.052	2.32
1220 dry " "		4.439	4.422		
1220 saturated with water		4.407	4.401		
1220 dried again		4.438	4.461		
5406		8.55	8.57		
424		5.00	4.98	5.04	5.06

It is confidently believed that the methods here described for the determination of chlorine in bromine and bromides are a practical solution of this old analytical problem, suitable for routine analyses of either technical or scientific character and adapted to replace the indirect methods.   It is a pleasant duty here to express my obligations to Dr. Carlton for his able assistance in the work.
St. Louis.

A CONVENIENT AIR-BATH AND HOT PLATE.

By EDWARD DeMILLE CAMPBELL.

During the past ten years the small combined air-bath and hot plate to be described has been in use in this laboratory and has proved so conven-