SEPARATING IODINE FROM CHLORINE AND BROMINE. 1051

LXXIV.—*A Quantitative Method of separating Iodine from Chlorine and Bromine.*

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WHEN heated with sulphuric acid and potassium dichromate, most iodides are decomposed, yielding iodine and a sulphate of the metal; silver iodide, however, is an exception, as, although it gradually dissolves, no iodine is separated, and, on diluting the solution and allowing it to cool, a yellow precipitate is deposited, consisting of impure silver iodate. This precipitate always contains chromium (possibly as chromiodate), which cannot be completely removed by

washing, and, on igniting it, some iodine is set free along with the oxygen. A weighed quantity of the precipitate was digested with dilute sulphurous acid to convert it into silver iodide, and the latter was collected and weighed as usual; the filtrate was greenish, from the presence of chromium, and contained also traces of silver, but no iodine. The percentage of iodine found in one sample was 43·27, in another 43·84; as silver iodide contains 44·88 per cent. of iodine, the precipitate is essentially silver iodate.

In order to leave no doubt as to its composition, a portion was purified by dissolving it in dilute ammonia, filtering from a slight, yellow, flocculent residue, and then reprecipitating by the addition of dilute sulphuric acid in excess. After this treatment, the precipitate was almost white and free from chromium. On igniting it, no iodine was liberated, but the compound split up quantitatively into oxygen and silver iodide, as the following experiments show.

0·6333 on ignition gave 0·5250 I. I = 44·80.

1·0355 „ „ 0·8623 I. I = 44·87.

AgIO₃ requires 44·88 per cent. I.

The action between silver iodide, potassium dichromate, and sulphuric acid may, therefore, in all probability, be expressed by the equation

Silver chloride and bromide, as might be expected, give no chlorate or bromate when heated with a mixture of potassium dichromate and sulphuric acid, but the chlorine or bromine is evolved in the free state, the silver remaining as sulphate.

On these observations, I have founded a method of quantitatively separating iodine from chlorine and bromine, which will, I believe, be found to have advantages over any of the methods at present in use.

The chlorine, bromine, and iodine are precipitated as silver salts in the usual way, and the precipitate is allowed to settle completely; it is then collected and thoroughly washed by decantation, the washings being passed through a small filter. The filter is in turn thoroughly washed, and is then spread out on a flat glass plate, and the small portion of the precipitate adhering to it is washed back into the beaker containing the bulk of the precipitate, as little water as possible being used. The hardened filters now sold will be found convenient for this operation, as their smooth surface readily allows the whole of the precipitate to be removed without any fibres of paper accompanying it; and this is important, as if any organic

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matter be allowed to mix with the precipitate, it will cause loss of iodine in the next operation. To the precipitate, about 2 grams of powdered pure potassium dichromate is now added, and then 15 c.c. of strong pure sulphuric acid in small portions. The beaker is covered with a watch-glass, and heated on the sand-bath until all the water has been boiled off, and white fumes of sulphur trioxide begin to be evolved. There is no tendency to "bumping" unless too much water has been added.

The silver iodide will now have been completely oxidised to iodate, whilst any chlorine or bromine will have been evolved as such. The liquid is allowed to cool somewhat, and cautiously diluted with *hot* water, in order to prevent the precipitation of silver iodate. To the clear, green solution, which, in ordinary cases, should measure about 150—300 c.c., a strong solution of sulphurous acid is now added in large excess. This precipitates the silver as iodide, but, to ensure complete precipitation, the solution should be warmed for some time. The precipitate is allowed to settle, and more sulphurous acid is added, to make sure that the reduction is complete. Finally, the precipitate is collected, washed, dried, ignited, and weighed as usual. In washing the precipitate, it is advisable to first pour off the clear liquid through a filter, and then to boil the precipitate with a rather large volume of dilute nitric acid, and to repeat this operation three or four times. If this precaution be omitted, the precipitate is apt to retain traces of sulphate.

The following table of results obtained by this method will serve to show its accuracy.

Weight of iodine (as KI) taken.	Weight of bromine (as KBr) taken.	Weight of chlorine (as NaCl) taken.	Weight of iodine obtained as AgI.	Percentage of iodine used obtained as AgI.
0·2708	—	0·1017	0·2701	99·74
0·4370	0·2564	—	0·4334	99·18
0·2282	0·4000	0·0710	0·2281	99·96
0·2282	—	0·1775	0·2291	100·38
0·2282	0·2000	—	0·2277	99·78
0·2282	0·2000	0·0355	0·2289	100·31

It is evident that the method can be easily extended to the determination of chlorides, bromides, and iodides, in a mixture containing all three. For this purpose, two portions of the solution are taken, and the chlorine, bromine, and iodine are precipitated from both by the addition of silver nitrate in excess.

The total weight of the silver haloids precipitated from one portion

is determined, whilst the precipitate obtained from the second portion is treated as described above with potassium dichromate and sulphuric acid, and the iodine is weighed as silver iodide. The filtrate from the silver iodide contains the silver which was originally present in the silver chloride and bromide, and this is precipitated and weighed as silver chloride. All the data required for calculating the weight of each element present are thus obtained. The weight of silver iodide subtracted from that of the chloride, bromide, and iodide together gives the weight of the chloride *plus* bromide. As the weight of silver in these is known, the proportion of chlorine to bromine can be readily calculated in the usual way.

The following is an example of an actual analysis:—10 c.c. of a solution containing 6·0698 grams of potassium iodide, 7·3534 grams of potassium bromide, and 3·6297 grams of potassium chloride in 250 c.c. was precipitated by silver nitrate; the mixed chloride, bromide, and iodide of silver weighed 1·0836 grams. The iodine was determined in another portion of 10 c.c. 0·3416 gram of silver iodide was obtained. Hence, the silver bromide and chloride together weighed $1·0836 - 0·3416 = 0·7420$ gram. The silver in these was determined in the filtrate from the silver iodide by precipitation as silver chloride, and was found to be 0·4767 gram. Hence, the weight of chlorine was 0·0697 gram, and the composition of the mixture:—

	Found.	Calculated.
Iodine, per cent.	27·06	27·21
Bromine „	28·68	28·95
Chlorine „	10·22	10·11

The method will, I venture to think, be found easier and more convenient than any of those hitherto proposed for the determination of the three halogens, and probably also more accurate.