384. *Mercurous Perchlorate as a Volumetric Reagent for Chlorides and Bromides.*

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Mercurous perchlorate, in conjunction with bromophenol-blue as adsorption indicator, has been used as a volumetric reagent for chlorides and bromides, and found to give excellent results.

With bromophenol-blue as adsorption indicator, mercurous nitrate is well established as a volumetric reagent for chlorides and bromides (von Zombory, *Z. anorg. Chem.*, 1929, **184**, 237); it has the advantage over silver nitrate that it can be applied in acid solution. Mercurous perchlorate is now shown to give equally good results and to have certain advantages. Its solutions are reasonably stable when kept under appropriate conditions; they are easy to prepare, are free from interfering mercuric ions, and give sharp end-points which coincide exactly with the equivalent points.

Preparation and Standardisation of Mercurous Perchlorate Solution.—The preparation and properties of mercurous perchlorate have been described by Newbery (*Trans. Electrochem. Soc.*, 1936, **69**, 611), who suggested that it might replace silver nitrate as a bench reagent in qualitative analysis. The solutions used in this investigation were made by shaking the following materials vigorously together at intervals over a period of an hour: red mercuric oxide (22 g.), perchloric acid (*d* 1·5; 45 g.), water (50 c.c.), and mercury (30 g.). A few drops of the liquid were withdrawn from time to time, diluted, treated with sodium chloride, and filtered. When the filtrate from this test portion ceased to give the test for mercuric ions with hydrogen sulphide, the liquid was decanted or filtered from the excess of mercury and diluted to 2 l. Such a solution is approximately 0·1N.

The solution was standardised immediately by electrolytic determination of mercury, by potentiometric titration of sodium chloride by using the mercury electrode (Muller and Aarflot, *Rec. trav. chim.*, 1924, **43**, 874), by titration of pure sodium chloride and potassium bromide with bromophenol-blue, and by Andrews's method with potassium iodate. All these methods gave identical results. For the titration of sodium chloride and potassium bromide, the solution of the halide was diluted to about 100 c.c., ½ c.c. of bromophenol-blue (0·05% in water) added, and the mercurous perchlorate solution run in until the colour of the precipitate changed from creamy white to lilac. This colour change is produced by a small fraction of a drop, especially if the addition of the indicator is delayed till near the end-point.

Influence of acids and salts. Nitric, perchloric, and acetic acids have no effect on the accuracy of the titration if the total acid concentration does not exceed 0·04N.; higher concentrations inhibit the colour change. Sulphuric acid causes a high titre. Silver ions and mercuric ions are the only cations which affect the method, the latter reducing the titre by an amount proportional to their concentration. This is due to the removal of some of the halide ions as undissociated mercuric halide. Hence, mercurous perchlorate which is free from mercuric ions has a distinct advantage over mercurous nitrate. Apart from the anions of weak acids, which yield insoluble mercurous salts, sulphate ion is the only anion that interferes, as little as 10 mg. of sodium sulphate raising the titre by 1%. This effect is completely eliminated, however, by adding an excess of lead nitrate to the boiling solution. The lead sulphate need not be filtered off before titration, but precipitation in the cold gives low results.

Stability of Mercurous Perchlorate Solutions.—Solutions examined over a period of 4 months behaved differently according as they had been exposed to light or kept in the dark. The former underwent considerable decomposition into mercury and mercuric perchlorate; the iodate titre diminished steadily. The curious point, however, is that, in its behaviour towards sodium chloride, the solution showed an apparent increase of strength, which rose fairly rapidly during the first few days and then more slowly till after 4 months it had increased by 2·5%. The iodate titre had decreased during the same period by less than 1%. Evidently, mercuric ions affect the titre not only by binding halide ions but also by inducing premature adsorption of the indicator.

On the other hand, solutions kept in the dark were reasonably stable. The iodate titre decreased by 0·4% but the sodium chloride titre remained almost unchanged during the whole period, being only 0·1% low after 4 months. Keeping the solutions over mercury or increasing the concentration of free perchloric acid had no effect whatever.

Details of Method.—Dilute the solution of the halide to about 100 c.c. If sulphates are present, boil it, add 10—20 c.c. of lead nitrate solution (5%), and cool. Add a drop of bromophenol-blue, then ammonia or sodium carbonate till the indicator turns faintly blue, and titrate with 0·1 or 0·05N-mercurous perchlorate. Just before the end-point is reached, add 0·5 c.c. of bromophenol-blue and continue the titration till the colour of the precipitate changes to lilac.

Some Typical Analyses.—The above method was used to determine chlorine in some pure products and in some natural waters. With pure lead chloride and barium chloride the results obtained were excellent: $PbCl_2$ (Found: Cl, 25·48, 25·48. Calc.: 25·50%); $BaCl_2,2H_2O$ (Found: Cl, 29·01, 29·03. Calc.: 29·03%). The results for various natural waters are in the table, which also includes the results of check determinations made by other methods. The boiler water was almost black, but the addition of lead nitrate to remove the sulphate gave a colourless filtrate and there was no difficulty in getting a sharp end-point.

	Chlorine found.		
Method.	Gravimetric.	Mohr.	$HgClO_4$.
Sea water, %	1·935, 1·934	1·940, 1·941	1·937, 1·937
Well water, parts per 100,000	13·61, 13·58	13·9	13·4, 13·6
Boiler water, parts per 100,000	58·3, 58·3	60·2, 60·5	58·3, 58·4
Drinking water, parts per 100,000	—	2·2	2·1

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