156. *Mercurous Perchlorate as a Volumetric Reagent for Iron.*

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Mercurous perchlorate, like the nitrate, reduces the ferric thiocyanate complex to the ferrous state. The conditions have been determined under which the reagent can be used for the volumetric estimation of iron without the necessity for reduction. The method is simple and accurate and is applicable to a wide variety of materials. The reagent has the added advantage that it is stable over very long periods of time when kept under proper conditions.

Bradbury and Edwards (*J. Soc. Chem. Ind.*, 1940, **59**, 96T) have shown that mercurous nitrate reduces the ferric thiocyanate complex to the ferrous condition and have adapted this reaction for the direct titration of ferric ion without previous reduction; this is a notable advance on all other methods for the estimation of iron.

The remarkable stability of mercurous perchlorate solution and the fact that it is such an elegant reagent for the estimation of chlorides and bromides (J., 1937, 1824) prompted this attempt to extend its use. It was stated (*ibid.*) that mercurous perchlorate slowly loses its strength as measured by potassium iodate (Andrews's method), but it has now been established that this is not so: the apparent loss has been shown to be due to a trace of chlorine in one sample of hydrochloric acid used in the previous work. Solutions have, in fact, been kept over mercury in the dark for 7 years and have maintained their strength almost unchanged towards both sodium chloride and potassium iodate.

The present work confirms the observations of Bradbury and Edwards in general. Accurate determinations of ferric ion may be made with mercurous salts under certain conditions. A large excess of thiocyanate must be added to the ferric solution before the titration is commenced, but the amount needed depends on the total volume and on the acid concentration. Bradbury and Edwards used titrating volumes of the order of 20 ml., but the present work concerns volumes more usually employed in volumetric work, *i.e.*, 100—200 ml. For this volume, about 3—5 g. of potassium or ammonium thiocyanate is sufficient provided the solution does not contain more than about 5 ml. of concentrated sulphuric or nitric acid or 2—3 ml. of concentrated hydrochloric acid. Larger amounts of acid give high results, though their effect can be countered by increasing the amount of thiocyanate used or, better, by partial neutralisation. The high concentration of thiocyanate prevents the precipitation of insoluble mercurous salts; the disappearance of the red colour at the end-point is sharp.

However, although Bradbury and Edwards claim that the reaction is strictly stoicheiometric at the dilutions used by them, this is not so at these higher dilutions. In neutral and dilute acid solutions the amount of perchlorate needed is approximately 1% higher than is demanded by the stoicheiometric ratio. It is therefore essential to standardise the mercurous solution against a ferric solution of known strength, containing a known amount of acid. Under these conditions the method is accurate and very simple.

EXPERIMENTAL.

Solutions required.—Mercurous perchlorate was made as previously described (*loc. cit.*) and found to be 0·1010N when standardised against both sodium chloride and potassium iodate. Ferric alum solution was made exactly 0·05M from " AnalaR " salt and this concentration was confirmed by standard dichromate and permanganate.

Titration of Ferric Solution with Mercurous Perchlorate.—Preliminary titrations confirmed Bradbury and Edwards's finding that reproducible results can be obtained only when a large excess of thiocyanate is added before the titration is commenced. Accordingly, 5 g. of potassium thiocyanate were added to 20 ml. of the ferric solution diluted to 150 ml., and the mercurous perchlorate was run in until the red colour was discharged (Found: 19·98 ml., whence $HgClO_4$ = 0·1001N). The low factor is probably due to some decomposition of mercurous thiocyanate into mercury and mercuric thiocyanate, because a grey precipitate formed during the titration and disappeared on shaking; but the solution, though colourless at the end-point, was never quite clear. Nevertheless, titration values could be duplicated exactly if the flask was well shaken during the titration.

Effect of acids. Addition of 5 ml. of concentrated mineral acid tended to raise the titre, the effect being most marked with hydrochloric acid. Partial neutralisation with ammonia or sodium hydroxide, however, corrected this tendency effectively. Additions of 2—3 ml. of these acids had no sensible effect. Phosphoric and acetic acids and their salts gave high results and indistinct end-points.

Effect of temperature. Near the end-point the reaction was slow and titres were always high unless several minutes were allowed between drop additions. In hot solution the results were erratic, being 20—40% low. Best results were obtained when the mercurous solution was added to the cold solution until the dark red colour faded to a light orange, 4—5 drops from the end-point, and the titration was finished at 60—70°.

Effect of ferrous ion, and titration of mixtures of ferrous and ferric ions. Addition of ferrous sulphate, free from ferric salt, had no effect whatever on the titre. Accordingly, a mixed solution of ferrous ammonium sulphate and ferric alum was made from " AnalaR " materials and analysed as follows. In one aliquot the ferric ion was estimated by the above method, and in a second, the ferrous ion was estimated by boiling with bromine water to oxidise it to ferric ion and titrating the total ferric ion in the same way. The results agreed with the calculated values and also with those determined by the conventional dichromate method, using stannous chloride as reducing agent.

Application to Analysis of Ferro-materials.—The table gives a comparison of the iron content of various materials as determined with mercurous perchlorate and with potassium dichromate (stannous chloride reduction, ferricyanide indicator). To emphasise the freedom of the method from interference by common impurities and by methods of bringing the material into solution, the following brief details are given. The oxide ores were dissolved in concentrated hydrochloric acid, in some cases with the aid of stannous chloride followed by oxidation with bromine. The steel was dissolved in hydrochloric acid, the solution filtered to remove carbon, and oxidised with bromine. The pyrites sample was decomposed with concentrated nitric acid and potassium chlorate and boiled down three times with hydrochloric acid to decompose excess chlorate and nitrate. The bauxite was decomposed with hot concentrated sulphuric acid, the solution diluted, treated with ammonia to precipitate iron and aluminium, etc., and the precipitate dissolved in hot hydrochloric acid. In all cases the titrations were made according to the following directions which have been found most satisfactory: the solution was diluted to 100—150 ml.; if the amount of hydrochloric acid exceeded 3 ml. of the concentrated acid it was partly neutralised with ammonia; potassium thiocyanate was then added, and the titration carried out as above. The mercurous solution was standardised as above.

	Fe, %, found by—	
	$K_2Cr_2O_7$.	$HgClO_4$.
Oxide ore, No. 1	53·62	53·60
,, No. 3	53·76	53·90
,, No. 4	58·80	58·66
,, No. 5	51·66	51·66

	Fe, %, found by—	
	$K_2Cr_2O_7$.	$HgClO_4$.
Steel	90·7	90·7
Pyrites	42·0	41·92
Bauxite	13·52	13·60

These results show that the method is accurate. It is simple and would seem to be particularly useful for dealing with steels and other materials which contain other reducible metals which limit the application of the Jones reductor and amalgam reductors.

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