

CLXXVII.—*Two Volumetric Methods for the Determination of Chromium.*

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## I.

WHEN ammonium persulphate is added to a solution of a chromium salt in the presence of silver nitrate and nitric acid, the chromium is oxidised to chromic acid.

Upon this reaction, H. E. Walters (*J. Amer. Chem. Soc.*, 1905, **27**, 1550) bases a method for the determination of chromium in steel. In this case, the manganese present is converted into permanganic acid, and the chromium into chromic acid. These two are estimated together by means of ferrous sulphate solution, and the permanganic acid alone by means of sodium arsenite.

This method, although capable of giving good results, has the objection that the chromium is determined by difference, and an appreciable error may thus be introduced where only small quantities of chromium are present.

Kleine (*Stahl und Eisen*, 1905, **25**, 1305; 1906, **26**, 396) removes manganese by first treating a solution of steel in nitric acid with persulphate alone. The manganese is thus converted into manganese dioxide, and may be filtered off. He then removes iron

by extracting the solution with ether, and estimates chromium in the aqueous solution by the persulphate-silver nitrate method.

This process is long, and the removal of the iron appears to us to be a superfluous operation.

The following process has been found to give trustworthy results, and it requires a minimum of time for its performance.

If manganese is absent, the solution is acidified with nitric acid and 20 c.c. of a 1 per cent. solution of silver nitrate added. To this mixture, about 10 grams of ammonium persulphate are added, and the solution boiled for five minutes. The chromium is thus converted into chromic acid, and the excess of the persulphate is decomposed. In order to make quite certain that no persulphate exists in this solution, a few c.c. of a dilute solution of manganese sulphate are now added. If persulphate is present, permanganic acid will be formed, and this may be decomposed by adding a dilute solution of hydrogen peroxide, drop by drop, until the permanganate colour just disappears. (A large excess of hydrogen peroxide must not be used, or reduction of the chromate may occur.)

The solution is once more brought to the boiling point, to expel oxygen, and then cooled and diluted. An excess of standard ferrous sulphate solution is now added, and the excess titrated back with standard dichromate solution. From the data so obtained, the amount of chromium may be calculated.

In the determination of chromium in iron and steel containing manganese, the process is as follows. Two grams of the iron or steel are dissolved in as little nitric acid as possible, and silver nitrate and persulphate added in the usual way. The solution is boiled for a few minutes, and a quantity of ammonium chloride solution is added, such that nearly all the silver is precipitated as chloride. On boiling, the permanganic acid is partly converted into manganese chloride and partly decomposed with the formation of hydrated oxide of manganese. The solution is now diluted to a definite volume, and filtered through an asbestos filter. A quantity of the filtrate, equal to one-half the original volume of the solution, is taken and treated in the same manner as described in the preceding process. The fact that silver nitrate is present in excess during the whole of the process, precludes the possibility of free chlorine being present in the solution.

In making up the solution to a definite volume, no account is taken of the volume of the precipitate, but, as the percentage of chromium present in iron and steel is comparatively low, no appreciable error is introduced on this account.

By working with sufficiently dilute standard solutions, the merest traces of chromium may be accurately determined by this method.

Instead of using a solution of ammonium chloride, a dilute solution of hydrogen peroxide may be employed to reduce the permanganic acid.

We attempted to estimate manganese and chromium in steel simultaneously by converting into permanganic and chromic acids respectively, and then titrating the former with hydrogen peroxide until the pink colour disappeared, whereupon the chromic acid remaining was titrated with ferrous sulphate solution.

The results obtained were, however, untrustworthy, since oxidation of the chromic acid to perchromic acid began before all the permanganic acid was reduced by the hydrogen peroxide.

### EXPERIMENTAL.

A solution was made of two grams of chromium-free steel in nitric acid, and to this, 10 c.c. of a solution of chromium sulphate were added. (1 c.c.=0.003 gram of chromium.)

After oxidation, 28 c.c. of ferrous sulphate were added. On titrating back with potassium dichromate solution (1 c.c.=0.003 gram of chromium), 1.2 c.c. were required. Ten c.c. of the potassium dichromate solution were equivalent to 24.8 c.c. ferrous sulphate solution:

Found, Cr=0.0302 gram.

Used, Cr=0.0300 gram.

Varying amounts of chromium were taken, and equally good results were obtained.

### II.

#### *Oxidation by Means of Sodium Bismuthate.*

When sodium bismuthate is added to a solution of a steel containing chromium, the chromium is oxidised to chromate. This reaction takes place instantly if the solution is boiled. At the same time, the manganese is converted into permanganic acid (Ibbotson and Brearley, *Chem. News*, 1901, **84**, 247, 269). On boiling, the manganese is precipitated as manganese dioxide.

We have obtained excellent results by proceeding in the following manner. Two grams of the iron or steel are dissolved in nitric acid, and about 3 grams of sodium bismuthate added in small quantities. The solution is then boiled until all the manganese is precipitated as dioxide. A small quantity of very dilute hydrochloric acid is now added, whereupon the manganese dioxide is dissolved. Excess of silver nitrate is then added, and the solution boiled, when silver chloride is precipitated. The solution is filtered through an asbestos filter, and titrated in the usual way.

## E X P E R I M E N T A L.

A solution was made of 2 grams of chromium-free steel in nitric acid, and to this, 20 c.c. of a solution of chromium sulphate were added. (1 c.c.=0.003 gram of chromium.)

After oxidation, 51 c.c. of ferrous sulphate solution were added.

The excess of ferrous sulphate required 0.5 c.c. of potassium dichromate solution. (1 c.c.=0.003 gram of chromium):

Found, Cr=0.0602 gram.

Used, Cr=0.0600 gram.

Equally good results were obtained with smaller quantities of chromium.

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