DETERMINATION OF NICKEL AND CHROMIUM IN STEEL.

BY EDWARD DeMILLE CAMPBELL AND WALTER ARTHUR.
Received May 6, 1905.

In February, 1895, one of the authors in conjunction with W. H. Andrews, published a method for the determination of nickel in nickel steel,[1] in which the nickel was determined electrolytically or by titration with potassium cyanide, using silver iodide in suspension as an indicator. About six months later Thomas Moore published his article "The Volumetric Estimation of Nickel"[2] in which he showed that the use of silver iodide as an indicator renders the cyanide titration of nickel sharp and accurate. Credit for the cyanide titration of nickel by the use of silver iodide as an indicator is usually given to Moore and undoubtedly this modification was worked out independently. In most of the materials analyzed by Moore the proportion of iron to nickel was comparatively small. He makes the statement towards the latter part of his article that "In presence of alumina, magnesia or ferric oxide, citric acid, tartaric acid or pyrophosphate of sodium may be employed to keep them in solution."

A number of volumetric methods based upon the cyanide titration of nickel using silver iodide as an indicator have appeared since the above were published. Most of these methods aim either to remove the iron before titrating for nickel or to add some reagent which will keep the iron dissolved when the solution is rendered alkaline.

H. Brearley[3] precipitates the iron in rather strongly acid acetate solution as basic acetate and titrates the nickel in an aliquot part of the filtrate, while G. T. Dougherty[4] precipitates iron as ferric hydroxide by means of a large excess of ammonia in presence of a strong solution of ammonium chloride. His results seem to show that if sufficient ammonium chloride be added, the ferric hydroxide will not contain any nickel, so that the titration of the aliquot portion of the filtrate will give accurate results.

As early as 1899, G. W. Sargent[5] described a combination of the now well-known ether method for the separation of iron with the cyanide-iodide titration for nickel. This combined method has been quite satisfactory in many ways, but where a large number of determinations are being made, the expense of the ether combined with the danger of fire attending its use and the disagreeable effect of inhaling the vapors, render the use of the ether method not entirely satisfactory.

[1] This Journal, 17, 125.
[2] Chem. News, 72, 92.
[3] Ibid., 74, 16.
[4] Iron Age, April 25, '07.
[5] This Journal, 21, 854.

The latest modification of the cyanide-iodide method for nickel in steel is that proposed by C. M. Johnson.[1] Johnson describes the cyanide-iodide method as that of T. Moore, although this method appeared in this country some six months in advance of the latter's article.

In the method proposed by Johnson, which is a modification of that given by Brearley and Ibbotson in their "Analysis of Steel Works Materials," page 183, the iron is kept in solution in the presence of a little free ammonia, by means of a large amount of citric acid, instead of a small amount as recommended by the above authors. By using 12 grams of citric acid per gram for ordinary nickel steels and 24 grams in case of chrome-nickel steels, the color of the solution is rendered light enough to observe the silver iodide without difficulty.

Johnson has shown that the amounts of vanadium, tungsten, molybdenum and manganese found in commercial steels do not interfere with the titration of nickel and that the dark color due to the presence of chromium may be partially overcome by the use of an increased amount of citric acid.

Experiments made in this laboratory with the method described by Johnson showed that even in the presence of large amounts of ammonium citrate, the brownish color of the ammoniacal solution did not permit as satisfactory a titration of nickel to be made as desired. We have endeavored, therefore, to see whether the use of sodium pyrophosphate to keep iron in solution would not give better results than the ammonium citrate.

In his original publications, Moore gave no details concerning the use of sodium pyrophosphate, since in the materials on which he worked the amount of iron present was not large enough to cause any trouble. In applying the method to the analysis of steel, some care is required to obtain conditions, such that the color of the solution will not be dark enough to cause any uncertainty as to the end reaction. The following method has been worked out and found to give satisfactory results in this laboratory.

One gram of the steel is dissolved in a casserole with 10 to 15 cc. of nitric acid (sp. gr. 1.2) with the addition of a little hydrochloric acid if necessary. After solution of the steel, 6 or 8 cc. of sulphuric acid (1:1) are added and the solution is evaporated until the sulphuric anhydride fumes begin to come off. Thirty to 40 cc. of water are now added and the solution heated nearly to boiling or until the ferric sulphate is all dissolved. The solution is then transferred to a 400 cc. beaker. In case the solution in the casserole is not perfectly clear but contains a little silica or carbon in suspension, it should be filtered so that the solution in the beaker is perfectly clear and bright. To the sulphuric

[2] THIS JOURNAL, 29, 1201.

acid solution in the beaker, which should be about 60 or 70 cc. in volume, are added 13 g. of sodium pyrophosphate previously dissolved in about 60 or 70 cc. of water heated to about 60° or 70°. After the addition of the sodium pyrophosphate, the solution containing the heavy white precipitate of ferric pyrophosphate is cooled to room temperature, and dilute ammonia (1 : 1) is added drop by drop, while the solution is vigorously stirred, until the greater portion of the pyrophosphate has dissolved and the solution has assumed a greenish tinge. The solution at this point should have an alkaline reaction towards litmus, but it should not smell of free ammonia. The solution is now warmed gently and stirred, when the remaining pyrophosphate will completely dissolve, giving a perfectly clear light green solution. If the ammonia is added too fast or the solution is not carefully stirred, a brownish color is apt to result but this can usually be overcome by carefully adding a few drops of dilute sulphuric acid. The clear light green solution is now cooled to room temperature and 5 cc. of silver nitrate (made by dissolving 0.5 g. of silver nitrate in 1000 cc. of water) are added, followed by 5 cc. of a 2 per cent. solution of potassium iodide. Standard potassium cyanide is now run in until the clearing up of the solution shows that the nickel has been completely converted into potassium nickel cyanide and the silver iodide into potassium silver cyanide. Before calculating the amount of nickel present, correction must be made for the amount of potassium cyanide required for the 5 cc. of indicator used.

The potassium cyanide used may be decinormal, made by dissolving about 13 g. of potassium cyanide in 1000 cc. of water and standardizing by direct titration with standard decinormal silver nitrate. If decinormal potassium cyanide is used, since the titration of the nickel takes place according to the equation $NiSO_4 + 4KCN = K_2Ni(CN)_4 + K_2SO_4$, the decinormal factor of metallic nickel will be 0.002935. If preferred, the potassium cyanide may be standardized against a nickel solution of known strength.

The above method gives very satisfactory results with nickel steels not containing chromium or copper.

If copper is present in amounts not exceeding 0.4 per cent., the amount of potassium cyanide required for the copper will not be as great as it would for an equal per cent. of nickel, but the copper will replace almost exactly $^3/_4$ of its weight of nickel. Thus if a sample contained 0.12 per cent. of copper, it would require an amount of potassium cyanide equivalent to 0.09 per cent. of nickel. In almost all cases of nickel steels containing copper, if the sample is dissolved in a covered Erlenmeyer flask in 25 cc. of water to which is added 5 cc. of sulphuric acid (sp. gr. 1.84), the nickel will all go into solution and the copper will remain undissolved. The solution is cooled and the undissolved copper is filtered out. The

ferrous sulphate in the filtrate is oxidized by the addition of a slight excess of hydrogen peroxide and the excess of this latter is boiled off. The solution is concentrated if necessary, and the method continued as in the case of nickel steel containing no copper.

In the case of chrome-nickel steels the sample is dissolved and converted into sulphate as described in the first method.   After dissolving in the casserole in about 40 to 50 cc. of water, the solution is brought to boiling and a 2 or 3 per cent. solution of potassium permanganate is added drop by drop to the boiling solution until a slight permanent precipitate of manganese dioxide is obtained.   The chromium in this way is readily oxidized to chromic acid much as in the well-known Galbraith process for the determination of chromium.   The solution is now cooled to room temperature, filtered, and the filtrate and washings concentrated in a 400 cc. beaker to about 60 cc.   Sodium pyrophosphate is added and the process continued as in the first instance when chromium is not present.   By oxidation of chromium to chromic acid, the dark color due to the presence of chromic salts is avoided and the chromic acid takes no part in the titration of the nickel.   The clear solution to which silver nitrate is added, will have a yellow rather than a green color when chromium is present, but no trouble is experienced in obtaining a sharp end reaction.

In case of chrome-nickel steels, the chromium may be advantageously determined in the same sample as that used for the determination of the nickel.   The solution of the sulphates in which the chromium has been oxidized to chromic acid, must be cooled thoroughly before filtering if filter paper is used, in order to avoid any reduction of the chromic acid by the paper.   To the clear solution of the sulphates containing chromic acid, an accurately weighed amount, usually 0.7 g., of ferrous ammonium sulphate is added and the excess of ferrous sulphate oxidized by means of standard potassium permanganate.

In order to obtain an accurate titration by means of potassium permanganate in the presence of chromic sulphate, it is best to weigh out the ferrous ammonium sulphate and reserve a small portion to be added after the pink color of the permanganic acid, usually indicating the end reaction, has been obtained.   The reserved portion of the ferrous ammonium sulphate is then added and the titration continued, employing, however, potassium ferricyanide as an external indicator as in the titration of iron by means of potassium dichromate.   Since the green chromic sulphate is partially complementary to the red permanganic acid, the color of this latter which usually indicates the end reaction will not be visible until too large an excess has been run in.   From the weight of the ferrous ammonium sulphate used and the amount of the decinormal potassium permanganate required, the per cent. of chromium may be

readily calculated as in the well-known methods for the volumetric de-
termination of this element. When chromium has been determined,
the solution is again brought to the boiling point. and the chromium
again oxidized to chromic acid by the addition of a 2 per cent. solution
of potassium permanganate until a slight permanent precipitate of man-
ganese dioxide is obtained. The solution is again cooled until cold and
the manganese dioxide filtered out and the method continued as though
the chromium had not been determined. If more than one gram of
ferrous ammonium sulphate has been used. 1 or 2 g. additional sodium
pyrophosphate should be added.

UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN.
April 24, 1908.

THE INFLUENCE OF FINE GRINDING ON THE WATER AND FERROUS-IRON CONTENT OF MINERALS AND ROCKS.

It has been the general practice, following the directions of numerous
writers, to reduce most rock and mineral powders to a very fine state
of division preliminary to their analysis. This seemed called for on several
grounds—to secure a proper sample of an inhomogeneous mixture, the
need of extreme fineness for the ferrous iron determination, for that of
the alkalies by the J. Lawrence Smith method, for all decompositions
that involve the use of boric oxide or lead oxide, and in general in order
to insure complete and speedy decomposition by fusion with an alkali
carbonate. A very fine powder is, however, far less needed for the last-
named purpose than has been commonly supposed. The writer's recom-
mendation has been to prepare a main sample of moderate fineness and
to grind separate small portions of this finer when needed.

Now comes the Swedish chemist, Robert Mauzelius, and shows[1] that
fine grinding is highly detrimental in the case of minerals containing
ferrous iron because of its resulting oxidation. Led by Mauzelius's work,
Nicholas Knight has shown that siderite oxidizes when finely ground.[2]
A. L. Day and E. T. Allen had shown how very great is the effect of fine
grinding on the moisture content of minerals[3] and Mauzelius in the paper
cited adds to our knowledge on this point by quantitative data with
respect to rock powders. These writers clearly show that coarse powders
entirely free from hydroscopic water. or containing but a few hundredths
of one per cent. of it, take up moisture progressively as the grinding

[1] Sveriges Geol. Undersökning Arsbok. 1 (1907), No. 3.

[2] Chem. News, 97, 122.

[3] Pub. Carnegie Inst., No. 31, pp. 56–7: Am. J. Sci., 19, 93; Bull. U. S. Geol.
Survey, 305, p. 55.