

very considerable size may be formed. Fig. 3 shows a spoon which has been annealed in water gas and then plunged into the tip of a large Bunsen flame. The figure is of the natural size.

It was thus made evident that in order to successfully anneal the ware, not only must the penetration of oxygen be prevented but also the penetration of reducing gases. Experiment showed that hydrogen, methane, acetylene, etc. were very active in producing blisters, while nitrogen and carbon dioxide were entirely inert. Carbon monoxide lay between the two extremes. Further work indicated that the most desirable atmosphere from a technical point of view was one which contained enough reducing gases such as hydrogen, methane, or carbon monoxide, to prevent the penetration of the small amount of oxygen which cannot be excluded when working with large furnaces, and enough inert gas, such as carbon dioxide or nitrogen, to prevent the penetration of the reducing gases. Such an atmosphere can be prepared in an apparatus such as is employed in making so-called producer gas, when so operated as to deliver a product consisting approximately of two thirds carbon dioxide and nitrogen and one-third carbon monoxide, with a small amount of hydrogen. Annealing processes based on the above observations are now employed in practically all the large silver producing factories in America.

I wish to acknowledge the constant interest and support in this work received from Mr. C. E. Cole, President of the Towle Manufacturing Company, Silversmiths, Newburyport, Massachusetts, and from Mr. Martin Boyle, sometime chemist of the same firm.

THE RAPID DETERMINATION OF NICKEL IN THE PRESENCE OF CHROMIUM, IRON AND MANGANESE.

By C. M. JOHNSON.

Received May 17, 1907.

In applying the method of T. Moore¹ to the determination of nickel in steel, the directions given on page 183, Analysis of Steel Works Materials by Brearley and Ibbotson were followed: One gram of steel was dissolved in a 150 cc. beaker with ten cc. of concentrated hydrochloric acid diluted with an equal volume of water.

When action ceased ten cc. of nitric acid (1.20) were added and the contents of the beaker were boiled to about one half. 16 cc. of dilute sulphuric acid were poured into the solution and also three grams of powdered citric acid. The solution was stirred until the citric acid was dissolved, transferred to a 600 cc. beaker, and rendered faintly but distinctly ammoniacal.

The nickel was titrated with a standard solution of potassium cyanide

¹ Chemical News, 72, 92.

using a measured amount of standard silver nitrate and two cc. of a 20 per cent. solution of potassium iodide as an indicator. The deep red color of the citrate of iron greatly obscures the end point. The authors complain of this color and recommend the use of a condensing lens to cast a beam of light through the darkness. In the presence of chromium the writer found that a still more sombre gloom settled down over the close of the reaction. The authors mentioned, also state that this element retards the union of the cyanide and the nickel causing the recurrence of the cloud of silver iodide.

After struggling with the process for some time and always carefully separating the chromium, and with it the iron, in chrome steels, an attempt was made to dispel the darkness and also to avoid these tedious separations: Less citric acid per gram of steel was taken and the dark red shaded to blackness.

Naturally, the amount of citric acid per gram of steel was then increased, that is, six grams of citric acid per gram of steel were used and a marked improvement was noted. Still more citric acid caused a complete lifting of the shadows.

The following modified procedure was finally adopted for nickel steels after having been thoroughly tested with plain carbon steels to which known amounts of nickel had been added: Dissolve one gram of steel drillings in a 150 cc. beaker with 20 cc. of hydrochloric acid (1:1). When action ceases add ten cc. of nitric acid (1:20).

Reduce the volume of the solution to about 15 cc. keeping the beaker covered during the boiling. Remove the beaker from the fire and pour into it eight cc. of conc. sulphuric acid diluted with 24 cc. of water. The presence of the sulphuric acid is essential to a sharp end reaction between the cyanide standard and the silver iodide in the subsequent titration.

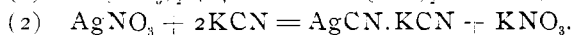
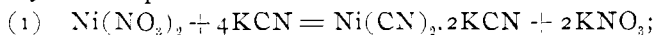
Transfer the contents of the beaker to one of 600 cc. capacity containing *twelve* grams of powdered citric acid. Stir until the citric acid is dissolved. Render this solution *faintly* but *distinctly* alkaline with ammonia, using one part of concentrated ammonia diluted with one part of water. A large excess of ammonia causes low results. Stand the beaker in running water until it is cold. The volume of the solution should now be about 300 cc. Much larger volumes than 300 cc. should be avoided as great dilution retards the end point causing the cloud of silver iodide to disappear and then to reappear again in a few minutes.

The faintly ammoniacal condition can be easily controlled by adding the ammonia rather slowly and noting the changes of color that ensue: The first change is to amber, then to yellowish green, then to distinct green, then to a light shade of green, then to a yellow almost matching

the yellow color of the acid solution. The reappearance of the yellow tint indicates that alkalinity is nearly attained.

A little more ammonia now causes a brownish shade which is evidence that the ammonia is in slight excess. The moderately alkaline citrate of iron obtained in the proportion of one gram of iron to 12 grams of the citric acid yields a bright greenish yellow solution in plain nickel steels instead of being of a dense dark red shade!

To the cold solution, two cc. of a 20 per cent. solution of potassium iodide are added. From a 50 cc. burette a standard solution of silver nitrate is dropped into the same beaker producing with the iodide a white turbidity. The standard potassium cyanide is added with constant stirring until the cloud of silver iodide just disappears which it does on being converted into silver cyanide. Nickel cyanide is first formed and then the silver cyanide is produced:



If the directions are followed as given, the titration can be accomplished at almost the full speed of the burette. If the titrated solutions are permitted to remain in the open beakers for a time a film usually appears on the surface of the liquid. No account is taken of it as its presence is most likely due to a superficial loss of ammonia. The reactions are always found to be completed when the body of the solution is freed of the iodide precipitate.

Standards—From the equations as given, 5.85 g. of silver nitrate are equivalent to 4.4868 g. of potassium cyanide. This weight of cyanide dissolved in one liter of water gives a value of one cc. equals about 0.001014 grams of nickel.

As comparatively little silver nitrate is needed with each analysis, it is not advisable to prepare more than a half liter of the water solution of this salt using 2.925 grams per 500 cc. of distilled water.

The potassium cyanide standard should contain about five grams of potassium hydroxide to the liter, which renders it quite permanent. The solutions are readily standardized by applying them to a plain steel to which a known amount of nickel has been added. The chemically pure double sulphate of nickel and ammonium is a convenient standardizing medium. For example 0.2 grams and 0.25 grams of the double sulphate can be weighed into 150 cc. beakers together with one gram of plain carbon steel drillings.

This mixture is then put through all of the foregoing manipulations and titrated with the cyanide solution that is to be standardized. The number of cc. of the silver nitrate and of the potassium cyanide solution used in this titration are noted. An excess of 10 cc. of the cyanide is now added and in turn titrated with the silver nitrate solution

until a distinct cloud of silver iodide is produced. This second titration gives the relation between the silver solution and the cyanide.

An actual case will illustrate the calculations: In sample No. 3477, 1.7 cc. of standard silver nitrate solution were required to produce a distinct turbidity and also to combine with any excess of potassium cyanide standard. In all 35 cc. of the cyanide were consumed in the titration. When the cloud of silver iodide had just been dispelled an excess of 9.8 cc. of cyanide was allowed to flow into the clear solution. Just 10.1 cc. of silver nitrate standard were needed to produce a reappearance of the cloudiness. Therefore $9.8 : 10.1 = 0.97$ or 0.97 cc. of cyanide standard solution equals 1 cc. of silver nitrate. Hence instead of deducting 1.7 cc. from 35 cc., 1.7×0.97 or 1.65 cc. were deducted leaving 33.35 cc. of cyanide combined with the nickel in this steel.

To a plain carbon steel 0.200 gram of double sulphate of nickel and ammonium were added put through all of the steps of a regular analysis. This mixture required 28.75 cc. of cyanide. The nickel salt contains 14.86 per cent. of nickel or $0.200 \times 0.1486 = 0.02972$ gram of nickel were present. Hence $0.02972 : 28.75 = 0.00103$ or 1 cc. of standard cyanide solution is equivalent to 0.00103 gram of nickel. No. 3477 as has been stated required 33.35 cc. of the cyanide standard, and therefore, contains $0.00103 \times 33.35 = 0.03435$ or 0.03435 gram of nickel or 3.435 per cent.

Chromium-Nickel Steels.—When chromium is present proceed exactly as in plain nickel steels except that twenty-four grams of citric acid per gram of steel are used. This proportion of citric acid is adequate to render the end point quite as easy to see as in ordinary nickel steels. The action is prompt and free from recurrence of turbidity. Of course, cloudiness through the entire solution will occur, as the ammonia is dissipated from it, after it has stood for some time in an open beaker.

The tabulation (1) that follows furnishes satisfactory proof that chromium does not interfere with the successful technical estimation of nickel in its presence:

Sample No.	No Chromium added Nickel found Per cent.	Per cent. of Chromium added to a portion of the same steels	Nickel found after the addition of varying amounts of Chromium
525	5.09	4.	5.10
2991	4.44	2.	4.45
7239	5.24	1.	5.28
3017	.96	1.	5.05
612	5.47	0.5	5.47
7273	5.29	1.	5.31
622	5.56	0.5	5.56
7288	5.32	2.	5.41
7289	5.11	2.	5.16
655	5.57	6.	5.59
2991	4.44	5.	4.47

The chromium was introduced in the form of recrystallized chemically

pure potassium dichromate. The dichromate crystals were mixed with a weighed amount of nickel steel drillings before the addition of the 20 cc. of hydrochloric acid. The combined action of the nascent hydrogen from the steel, the excess of boiling hydrochloric acid and the ferrous chloride reduced the chromate to chromic chloride, thus duplicating the conditions found when a chromium-nickel is similarly treated.

Determinations by this modification of the cyanide method can be finished in from 45 to 50 minutes, either in the presence or absence of any per cent. of chromium likely to be met with in steels or alloys soluble in the acids given. In this laboratory *duplicate* determinations in nickel or nickel-chromium steels are made in the time just specified. By the process one can decide in a few minutes whether or not nickel is present in a given steel and just how much. Tungsten, if present, does not interfere, appreciably, as has been noted by the authors mentioned in this article. The writer had two different amounts of nickel added to a steel containing several per cent. of chromium and 16-17 per cent. of tungsten. This steel was then carried through exactly as though no tungsten or chromium were present using the method as given for chromium-nickel steels.

Nickel added	Nickel found
0.0297 gram	0.0299
0.03715 "	0.0372
none	0.0006

Tests were then made in the same manner in the presence of molybdenum and vanadium as follow :

TABLE 2.

Name	Kind of steel or mixture	Nickel added Gram	Nickel found Gram
J. R. Steel	Contains 10 per cent. \pm Mo	0.0297	0.0295
"	" "	0.0222	0.0223
"	" "	none	0.0002
Bxx-173 Steel	Contains 4 per cent. Mo and 4 per cent. Cr	0.0223	0.0222
"	" "	0.0297	0.0296
"	" "	none	0.0004
A mixture	0.920 Gram of Steel	0.0297	0.0298
	0.030 " " Nickel		
	0.018 " " Vanadium		
A mixture	0.840 Gram of Steel	.0223	0.0227
	0.022 " " Nickel		
	0.035 " " Vanadium		
A blank	1.000 Gram of Steel	none	0.0008
	0.035 " " Vanadium		

Table 2 demonstrates that neither vanadium, tungsten, chromium nor molybdenum, when present in the amounts given, interferes, appreciably in technical analysis. These amounts represent extreme cases, especially for the vanadium, it being equivalent in one instance to 3.5 per cent. V when one gram of steel is taken.

As copper also forms cyanides, its presence would cause results to be

too high, but copper is religiously avoided in good steel making. Its presence is extremely unlikely in greater amounts than 0.06 per cent., although the writer, on one occasion, found as much as 0.25 per cent. in a low carbon steel, not a *crucible* steel, however. Crucible steel rarely contains over 0.04 per cent. copper. The choice brands are under 0.02 per cent. in copper.

Wishing to test the extent to which nickel could be titrated in the presence of large percentages of chromium, iron being also present, the mixtures as given in Table 3 were titrated with potassium cyanide. The various salts were weighed into 150 cc. beakers, together with the proper amounts of steel drillings. The same proportions of hydrochloric, nitric, citric and sulphuric acids were employed as are herein given for nickel-chromium-steels, and were applied in the same manner.

A sufficient quantity of the salts of chromium and nickel, and of the steel drillings were taken to give a total of one-half gram of metals in the mixture.

Double sulphate of nickel and ammonium ($(\text{NH}_4)_2\text{SO}_4 \cdot \text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), potassium dichromate and steel drillings free from nickel were used as sources of nickel, chromium and iron, respectively.

To obtain the nickel value of the cyanide standard under conditions similar to those existing in the mixtures tested, standardizing mixtures of these salts were prepared varying from the mixtures tested as much as 1 per cent. to 20 per cent. in the different constituents.

For mixtures exceeding 10 per cent. of nickel, a standard cyanide solution with a nickel value of 1 cc. = 0.0031 gram of nickel was used. The standardizing mixtures were dissolved and treated exactly as the mixtures tested. The same method of standardization was observed in the work recorded in Table 4.

TABLE 3.

Ni	Per Cent. of Metals.		Gram of Nickel.		
	Cr.	Fe.	Added.	Found.	
30	40	30	0.1499	0.1494	0.1495
60	20	20	0.2999	0.3003	0.2989
20	40	40	0.1029	0.1022	
5	90	5	0.0250	0.0248	0.0244
4	92	4	0.0200	0.0199	
1.5	95	3.5	0.00749	0.00805	0.00822
0.5	99	0.5	0.00249	0.00225	0.00245
0	98.9	1.0	None.	0.00247	0.0026
				None.	

Table 3 demonstrates that nickel may be estimated by the foregoing modified cyanide process, using the proportions of citric acid as given, with sufficient accuracy for works analysis, and indeed for most practical purposes; even when the percentage of chromium is as much as 99 per cent., and the nickel content is but one-half of one per cent.

The titration of the mixtures given in Table 3, and containing the larger amounts of chromium, requires considerable practice on the part of the operator. The work should always be carried out in duplicate. The disappearance of the cloudiness in the presence of 0.100 to 0.450 gram of chromium in a volume of 350-400 cc., is much more exactly observed when the mixture containing the iodide cloud is compared, from time to time, with a *similar* mixture which is perfectly free of this milky turbidity. The dilution of the deep purple, or wine color, of these ammoniacal mixtures of citrates to more than 300 to 400 cc., renders the end point but slightly more distinct, and has the great objection of retarding the reaction between the cyanide and the nickel. The increase above twenty-four grams of citric acid, in the solution, even to the extent of adding sixty grams of citric acid, did not relieve the density of color to any perceptible extent.

When titrating with a standard, 1 cc. of cyanide = 0.0031 gram of nickel (three times the strength used for steels) do not also increase the strength of the silver standard to equal it, but still retain the silver nitrate standard as given for steels. A silver nitrate solution sufficiently concentrated to be equivalent, volume for volume, to the cyanide standard (1 cc. = 0.0031 gram of nickel) on being dropped into the solution containing the potassium iodide, does not produce the usual opalescence, alone, but also forms curds of iodide that do not readily combine with the cyanide standard. The end point is reached and the main body of the solution is free of cloud while curds of silver iodide still lie on the bottom of the beaker. The weaker silver nitrate standard, or 5.85 grams of silver nitrate to the liter, produces with the potassium iodide a finely divided cloud of precipitate that combines promptly with the strong cyanide standard, giving a sharp end point. Weigh, therefore, 2.925 grams of silver nitrate, diluting to 500 cc., and 13.4604 grams of the best grade of potassium cyanide, diluting to 1000 cc., for titrations of solutions containing from 0.100 to 0.300 gram of nickel; 1 cc. of this silver nitrate solution should be equivalent to $1/3$ cc. of the concentrated cyanide standard (1 cc. cyanide = 0.0031 \pm grams of nickel).

The titration of nickel by potassium cyanide in mixtures containing large percentages of manganese with varying amounts of chromium and iron was also tried.

As in the experiments outlined in Table 3, mixtures were prepared to contain one-half gram of metallic substances. The same nickel and chromium salts were employed. Potassium permanganate crystals supplied the manganese.

The crystals of double sulphate of nickel and ammonium, potassium dichromate and potassium permanganate, were weighed into a 150 cc. beaker with the steel drillings. To this were added 20 cc. of dilute hy-

drochloric acid. The contents of the beaker were then boiled, after the first action was completed, until the chromate and permanganate were reduced. An addition of 10 cc. of nitric acid (1.20) followed, and the analysis was carried out exactly as given for chromium-nickel steels, using twenty-four grams of citric acid. The results obtained are given in Table 4. Sulphuric acid was added as in the process for steels.

TABLE 4.

Per cent. of Metals.			Gram of Nickel.		
Ni.	Mn.	Cr.	Fe.	Added.	Found.
41	20	10	50	0.2059	0.2058
20.6	40	20	20	0.1029	0.10228
15	60	15	10	0.0750	0.0752
1.5	95.5	1	2	0.00749	0.00762
0.25	94.9	2	2.9	0.00124	0.00122
—	94.9	2	4	None	0.00006

Table 4 gives evidence of the fact that nickel can be accurately determined in the presence of large percentages of chromium and manganese, if the conditions herein given are carefully observed. In the hands of a practised operator no difficulty was experienced in the analysis when as much as 95 per cent. of manganese was in solution with but 0.25 per cent. of nickel.

LABORATORY OF PARK STEEL CO. WORKS OF
THE CRUCIBLE STEEL CO. OF AMERICA.

THE DETERMINATION OF SILICA AND ALUMINA IN IRON ORES.

BY G. W. DEAN.

Received April 22, 1907.

Further experience with the method which was described in this Journal last year¹ has led to its modification in two or three important particulars. It has been found that the ore may be ignited directly instead of separating and igniting the residue from digestion with hydrochloric acid. It has also been found that a porcelain crucible is the most suitable for the ignition, since the ore is less liable to be overheated and the alumina rendered insoluble. When the determination of alumina is not required, the use of stannous chloride aids greatly in dissolving the ore. It has also been found that by heating the ore with sulphur it is partly reduced in such a manner that it is more easily soluble in hydrochloric acid and the whole method can be used when it is desired to determine both silica and alumina. The methods which are now used are as follows:

Determination of Silica Alone. Weigh 0.5 g. of the finely pulverized ore (100 mesh), transfer to a 20 cc. porcelain crucible, cover and heat over a Dangler burner until the contents of the crucible are dull red, raise the temperature for a few seconds and then remove the crucible from the source of the heat. The whole operation should take not more than two or three minutes. Transfer the ignited ore when cold to a beaker, add 20 cc. strong hydrochloric acid containing one gram of stannous chloride

¹ This Journal, 28, 882.