[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

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SINCE publishing his former method for the determination of nickel in nickel-steel (This JOURNAL, **16**, 96), the author has been endeavoring to perfect another method which should be an improvement over the first one. Such accurate results have been obtained in so short a time by this method that it is thought desirable to give the details of manipulation.

Place a one gram sample of nickel-steel in an Erlenmeyer flask of about one-half liter capacity. Add twenty-five cc. of nitric acid (1.20) and boil until dissolved and nitric oxide is boiled out of the flask. Meanwhile, dissolve thirteen grams of sodium pyrophosphate in seventy-five cc. of warm water. This solution must not be boiled as the pyrophosphate is thereby converted to the orthophosphate.

After complete solution, filter the sodium pyrophosphate and add it to the cooled solution of the steel. This will give a heavy, white precipitate of ferric pyrophosphate. Add, a little at a time, with constant agitation, a clear twenty per cent. solution of sodium carbonate until the precipitate of ferric pyrophosphate just dissolves and the solution attains a dull, olive-green color.

An excess of sodium carbonate must be carefully avoided, as the subsequent precipitation of nickel will not be complete if this is not done. With an excess of the carbonate the solution turns red, so that color may be used as a guide to the required amount. For a one gram sample, fifty to fifty-five cc. of twenty per cent. sodium carbonate is usually sufficient.

After redissolving with sodium carbonate, filter through asbestos, receiving the solution in a one-half liter Erlenmeyer flask; wash the filter with water sufficient to rinse out the original flask and to insure complete transference of the solution. Now add to the solution two grams of potassium xanthate freshly dissolved in twenty to twenty-five cc. of water. Stopper the flask and shake at frequent intervals for ten minutes. The nickel will be completely precipitated as xanthate, together with any copper the steel may contain, but perfectly free from manganese and almost free from iron. Filter as rapidly as possible through asbestos, using a pump, and wash the brick-red nickelous xanthate four or five times with freshly prepared one per cent. potassium xanthate.

The solution of potassium xanthate used for precipitating, as well as that used for washing, should be prepared by adding to the desired amount of salt sufficient water for solution, but should not be allowed to stand longer than fifteen or twenty minutes before using as it slowly decomposes. The dry salt is stable.

Dissolve the washed precipitate off the filter by allowing twenty cc. of freshly diluted fuming nitric acid to fall little at a time on it. The dilute fuming nitric acid should be prepared just before using by pouring ten cc. of water into ten cc. of fuming nitric acid. Catch the solution of the xanthate precipitate in a small Erlenmeyer flask. Wash the filter two or three times with hot water, then pass through five cc. of dilute sulphuric acid (2:3) and wash this out with more hot water. Boil the solution in the flask rapidly until the nitric acid is completely expelled and sulphuric anhydride fumes begin to rise. Cool, add twenty to twenty-five cc. of water, heat nearly to boiling, and, when all is in solution, pass in hydrogen sulphide for two or three minutes. Allow to stand until the cupric sulphide has settled. Filter and wash with hot water containing a little hydrogen sulphide.

Boil the filtrate, containing the nickel and a very small amount of iron, until hydrogen sulphide is expelled, add a few drops of hydrogen peroxide, or a few milligrams of sodium peroxide to oxidize the iron, and boil, then precipitate the iron with a very slight excess of ammonium hydroxide. Boil, filter, and wash once or twice with hot water. Dissolve the small precipitate of ferric hydroxide off the filter with five cc. of dilute sulphuric acid (2:3) and reprecipitate with a slight excess of ammonium hydroxide. Boil and filter into the original filtrate. This solution will contain all the nickel free from iron, manganese, and copper The nickel may be determined in either of the following ways :

1. *Electrolytically.*—Place the united filtrates from the ferric hydroxide in a platinum dish having a capacity of about 200 cc., add thirty cc. of a ten per cent. solution of disodium hydrogen phosphate, then twenty-five cc. of strong ammonium hydroxide. The solution should have a bulk of about 175 cc. Electrolyze for twelve hours with a current of 0.14 amperes per 100 sq. cm. area of the dish, having the electrodes about one-half cm. apart.

The precipitate of nickel obtained in this way is perfectly clear and bright, hardly to be distinguished from the platinum on which it is deposited.

Wash the precipitated nickel with warm water then with alcohol. Dry and weigh as usual. For accurate work it is more satisfactory to use a second platinum dish washed and dried like the first, as a counterpoise.

2. *Volumetrically.*—Place the united filtrates from the ferric hydroxide in a medium sized Erlenmeyer flask and cool until cold. The solution should have just enough free ammonia to give a slight but distinct odor; if this is not present at this stage, add a few drops of ammonium hydroxide. Add five cc. silver nitrate indicator (made by dissolving five-tenths gram silver nitrate in 1,000 cc. of water). Add five cc. of a two per cent. solution of potassium iodide, which give the solution an opalescence due to the presence of silver iodide in suspension.

Run in standard potassium cyanide (one cc. = 0.001 gram nickel) until the solution becomes clear and bright. The titration depends upon the fact that so long as there is any nickel uncombined with potassium cyanide in the form of the double cyanide, the silver iodide will remain undissolved, but as soon as the nickel has all been changed the silver iodide dissolves forming potassium silver cyanide and the solution becomes perfectly clear.

Subtracting a correction necessary for the titration of the indicator from the total amount of potassium cyanide used, gives the amount necessary for the nickel.

Standard Solutions Required.—Standard nickel solution : This can be most easily prepared from pure nickel wire. The commercially pure nickel wire usually contains 98.5–99.5 per cent.

nickel. If this wire is used for making the standard solution, take such a weight as will represent one gram of pure nickel, dissolve in a No. 3 beaker with twenty-five cc. nitric acid (1.42) and evaporate just to dryness on the water-bath. Moisten with a few drops of nitric acid, add about twenty-five cc. of water, and heat to solution. When the nickel is dissolved, dilute to fifty or sixty cc., add six grams of sodium acetate dissolved in a little water, heat nearly to boiling until the ferric basic acetate separates. Filter, and wash thoroughly with hot water. Add five cc. of sulphuric acid to the solution, transfer to a graduated liter flask, cool, and dilute to 1,000 cc.

Standard Potassium Cyanide.—Dissolve four and five-tenths grams of potassium cyanide in water and dilute to 1,000 cc. This must be standardized against the standard nickel solution.

Run in from a burette twenty-five to thirty cc. of the nickel solution into a medium sized Erlenmeyer flask, dilute with water to about 100 cc., add ten cc. of dilute sulphuric acid (2:3); then add ammonium hydroxide carefully until a slight but distinct odor of ammonia is perceptible. Add five cc. of silver nitrate indicator, five cc. of two per cent. potassium iodide and titrate with potassium cyanide until the solution brightens. Correction for the indicator is found by proceeding exactly as above, except that the standard nickel solution is omitted.

The potassium cyanide is quite stable, weakening, however, gradually on standing. The deterioration amounted from five-hundredths to one-tenth cc. in twenty-five cc. during one week.

In order to test fairly the accuracy of the recovery, the varying amounts of pure nickel wire were weighed and dissolved by my private assistant, who turned them over to Mr. Andrews as strictly unknown samples. Weighed amounts of iron wire were then added and the solution proceeded with as if it were an ordinary sample of steel.

Two hours is sufficient time to get the solution ready for electrolysis or for titration.

The following table will show the accuracy of the results obtained, where the amount of nickel present was strictly unknown to the operator until the analysis was completed:

Iron added. Grams.	Nickel taken. Gram.	Nickel recovered. Gram.	Gain and loss. + — Gram.	Method.
0.2105	0.08892	0.08910	+ 0.00018	Electrolytically.
1.0000	0.03430	0.03435	+ 0.00005	"
1.0041	0.05298	0.05345	+ 0.00047	"
1.0043	0.10824	0.10825	+ 0.00001	"
2.0043	0.02690	0.02740	+ 0.00050	"
1.0010	0.00100	0.00089	— 0.00011	Volumetrically.
1.0086	0.06578	0.06532	— 0.00046	"
1.0066	0.07582	0.07583	+ 0.00001	"
1.0057	0.08017	0.08050	+ 0.00033	"
1.0071	0.09389	0.09381	— 0.00008	"

ANN ARBOR, MICHIGAN,
December 18, 1894.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE ROSE POLYTECHNIC INSTITUTE. VI.]

THE VOLUMETRIC DETERMINATION OF PHOSPHORUS IN STEEL AND CAST IRON.[1]

BY W. A. NOYES AND J. S. ROYSE.

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IN a previous paper[2] one of us, with Mr. E. D. Frohman, showed that in the reduction of molybdic solutions by means of Jones' reductor, the molybdenum is reduced to a form corresponding to the oxide Mo_2O_3. We also showed that the reduced solution is very easily oxidized by exposure to the air, and we were led to believe this would account for the difference between the theoretical factor for the calculation of the phosphorus equivalent of a permanganate solution from its iron equivalent, and the empirical factor as given by Dudley and Pease.[3]

In a private communication, however, Dr. Dudley has very kindly called our attention to the fact that he obtained the same results when following the directions for reduction given in our paper as when following the method which he had previously used. As the difference between his results and ours corresponded to only three-tenths or four-tenths cc. of the permanganate solution used, and the results obtained by Mr. Frohman

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[1] Read at the Boston Meeting, December 28, 1894.

[2] This JOURNAL, 16, 553.

[3] This JOURNAL, 16, 230.