TABLE II.—THE EFFECT OF CHLORINE ON THE SENSITIVENESS OF THE METHOD.

Chlorine added.	Nitric nitrogen present.	Nitric nitrogen found.	Chlorine added.	Nitric nitrogen present.	Nitric nitrogen found.
0.5278	0.1	0.1	5.278	0.1	0.1
1.056	0.1	0.1	5.886	0.1	0.095
1.584	0.1	0.1	6.342	0.1	0.094
2.113	0.1	0.1	6.856	0.1	0.092
2.638	0.1	0.095	7.362	0.1	0.092
3.167	0.1	0.090	7.917	0.1	0.092
3.694	0.1	0.098	8.446	0.1	0.092
4.224	0.1	0.090	8.9776	0.1	0.090
4.749	0.1	0.090	9.496	0.1	0.086

Similar determinations were made until a concentration of thirty parts per million of chlorine was reached. No further decrease in the amount of nitric nitrogen found was obtained, *i. e.*, the amount of nitric nitrogen found tended to approach a constant value of nine-tenths of the amount actually present.

The results show that chlorine, when present in quantities as low as 2.638 parts per million, affects the results for nitric nitrogen obtained by this method, less nitric nitrogen being found than is really present.

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ON A NEW VOLUMETRIC METHOD FOR COBALT AND NICKEL.

BY GEORGE S. JAMIESON.

Received April 8, 1910.

The well-known application of potassium ferrocyanide to the volumetric determination of lead and zinc has led the writer to investigate the application of this method to the determination of cobalt and nickel, and conditions have been found under which concordant and accurate results may be obtained. As far as can be found by consulting the literature, this method has not been previously suggested.

It is believed that the most important practical application of the method will be in the determination of nickel in steel, for it can be carried out in the presence of iron, it is rapid and requires no expensive reagents. As far as ease and rapidity are concerned, it appears that the cyanide method as applied in the presence of iron by C. M. Johnson[1] and also by Campbell and Arthur[2] is the only one which can compete with it. The writer has found that by combining the modifications of the authors just referred to, the cyanide method may be decidedly improved, as will be shown by the description and the results which are given beyond. The choice between the ferrocyanide and the cyanide methods for nickel in steel would depend upon the preference of the operator, but it is to be observed that the cyanide method is not applicable to large amounts

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[1] THIS JOURNAL, **29**, 1201 (1907).

[2] *Ibid.*, **30**, 1116 (1908).

of cobalt on account of a peculiar dark precipitate produced under these circumstances during the cyanide titration which interferes with the end reaction.

For the ferrocyanide titration a solution containing 20 grams per liter of potassium ferrocyanide is recommended as a suitable strength for most work. Then each cubic centimeter will be equivalent to about 3 milligrams of cobalt or nickel. To standardize this it is best to employ a cobalt or nickel solution of known strength prepared either from pure salts in known volume, or by gravimetric standardization. Three equal portions of this solution containing about 0.1 gram of the metal are taken in beakers. Ten cc. of a 10 per cent. solution of ferric chloride and 2 to 3 grams of citric acid are added to each and then ammonia is added with stirring until the solution has a faint odor of the reagent. It is important that the excess of ammonia should not be too great, as in this case the results will be irregular. The solutions are then diluted to about 100 cc. with hot water and are brought to a temperature of 65–75°. The ferrocyanide solution is now run in slowly with constant stirring. After a few drops of the ferrocyanide have been added, the nickel or cobalt ferrocyanide begins to precipitate. As the titration progresses, a drop or two of the solution is removed by means of the stirring rod to a paraffined white plate and acidified with a drop of dilute acetic acid. The solution is thoroughly stirred and a second test is made in the same way beside the other. This pair of tests is designated as No. 1 and a record is made of the volume of ferrocyanide used at this point. The titration is carried on in this way until a greenish color is developed in about five minutes at a definite point in the series. The most convenient practice is to titrate the first portion roughly, and then to get the exact point with the other two portions. The important precautions are to avoid more than a slight excess of ammonia and to titrate slowly with thorough stirring.

The actual determinations are made in exactly the same way as the standardization just described. The method cannot be applied in the presence of such metals as copper, zinc, and manganese which react with potassium ferrocyanide. In the case of substances containing a considerable amount of iron, which must be in the ferric condition, no addition of ferric chloride is required.

The following results were obtained with varying quantities of cobalt and nickel solutions:

The following directions may be followed for the determination of nickel in steel: Weigh out 1.0000 gram of borings into a 150 cc. flask, add 10–15 cc. of dilute nitric acid (equal volumes of 1.42 sp. gr. acid and water). Cover the flask with an inverted crucible cover, and when the violent action is over, remove cover and boil gently over a free flame, keeping the flask in constant motion and inclined at about 45°, until the

1 cc. $K_4Fe(CN)_6$ soln. = 0.002105 gram Co, or 0.001885 Ni.

No.	Co taken. Gram.	cc. $K_4Fe(CN)_6$ used.	Co found. Gram.	Error.
1	0.0632	30.1	0.0633	+0.0001
2	0.0379	18.0	0.0379	±0.0000
3	0.0379	18.0	0.0379	±0.0000
4	0.0063	3.1	0.0065	±0.0002
5	0.0442	21.0	0.0442	±0.0000
6	0.0505	24.0	0.0505	±0.0000
7	0.0537	25.7	0.0541	+0.0004
8	0.0287	13.5	0.0284	—0.0003
9	0.0144	4.6[1]	0.0145	+0.0001
10	0.0144	4.6[1]	0.0145	+0.0001
	Ni taken.		Ni found.	
11	0.0462	24.5	0.0462	±0.0000
12	0.0770	40.8	0.0769	—0.0001
13	0.0770	40.8	0.0769	—0.0001
14	0.0377	19.8	0.0373	—0.0004

steel is decomposed. (If a steel is encountered which is not entirely dissolved by nitric acid, add a drop or two of strong hydrochloric acid or a crystal of potassium chlorate and continue the boiling.) Add 10 cc. of concentrated nitric acid as soon as the steel is in solution, heat to boiling again, and add half a gram of solid potassium chlorate. Boil until the chlorine is expelled. Add the same quantity of chlorate again and boil for about two minutes. Then allow the flask to cool a little and filter off the manganese dioxide on a Gooch crucible, washing with as small a quantity as possible of cold water. Proceed then according to the method already described. It is to be observed that the presence of a large amount of iron, as in the case of nickel steel, somewhat retards the appearance of the end reaction. It is advisable to standardize the ferrocyanide solution in the presence of about the same amount of iron as is present in 1 gram of steel. The following determinations were made in the three samples of steel by the method just described. The nickel in A was checked by the electrolytic, ether-cyanide, and dimethyl-glyoxime methods. The analyses of samples B and C were completed before the results by other methods were known.

No.	Ni steel. Grams.	cc. $K_4Fe(CN)_6$.	Per cent nickel.	Ni by other methods.
1A	1.0000	11.55	3.63	3.65
2A	1.0000	11.50	3.62	3.65
3A	1.0000	11.60	3.64	3.65
1B	1.0000	11.00	3.46	3.47
2B	1.0000	10.90	3.43	3.47
3B	1.0000	11.10	3.49	3.47
4B	1.0000	11.10	3.49	3.47
1C	1.0000	11.20	3.52	3.50
2C	1.0000	11.10	3.49	3.50
3C	1.0000	11.20	3.52	3.50

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[1] Another ferrocyanide solution.

Duplicate analyses of nickel in a steel can be made in this way in about an hour, and the results show that the method is accurate.

The following application of the cyanide method to the determination of nickel in steel was worked out by the writer before the papers of Johnson and Campbell and Arthur, which have been previously referred to, had been seen. The former investigator used a large amount of citric acid, while the latter used a large amount of sodium pyrophosphate. The writer uses both of these reagents together, but in much smaller quantity. The directions, according to the writer's modification, are as follows:

Take 0.5 gram of borings in a 150 cc. flask, add 10 cc. of 1 : 1 nitric acid and dissolve according to the directions given for the ferrocyanide method. If the metal contains more than 0.5 per cent. of manganese, the writer prefers to remove it according to the directions just referred to. Add to the nitric acid solution 2 to 3 grams of citric acid and 2 grams of anhydrous sodium pyrophosphate, then add ammonia slowly with stirring until the precipitate formed at first just dissolves and the solution acquires a very faint odor of ammonia. If too much ammonia has been used, it must be nearly neutralized by the careful addition of nitric acid. Dilute to about 150 cc. and cool to a temperature below 20°, add a few drops of a 10 per cent. solution of potassium iodide, and enough tenth-normal silver nitrate solution, the volume of which must be noted, to produce a distinct turbidity. Then run in potassium cyanide solution very slowly with stirring until the turbidity just disappears and the solution lightens to a golden yellow color. The solution should remain bright for five minutes, otherwise the titration is incomplete. Sometimes it happens that the turbidity disappears when only one-third to one-half of the required amount of cyanide has been used, but in this case upon the addition of a drop or two of silver nitrate, or upon waiting a moment, the turbidity reappears. The end-point is best observed when the beaker is placed upon a white paper having an elliptical hole in it under which is placed a black glazed paper for contrast. In making the calculation the proper deduction for the silver nitrate used should be made.

The potassium cyanide solution should be standardized by means of the tenth-normal silver nitrate. To do this take 20 cc. in a beaker, dilute to about 150 cc. with cold water, add ammonia until the odor is distinct but slight, add a few drops of 10 per cent. potassium iodide solution, run in silver nitrate until a distinct turbidity is produced, and then finish by slowly adding the cyanide solution until the turbidity just disappears. The theoretical amount of nickel per 1 cc. of tenth-normal solution is 0.002935 gram, but instead of using this value it is perhaps preferable to standardize the solution with a steel of known content in nickel.

The theoretical value was used in the test analyses given below, which indicate very satisfactory results for the method.

No.	Ni steel. Gram.	cc. KCN.	Per cent. nickel.	Ni by other methods.
1A	0.5000	6.70	3.70	3.65
2A	0.5000	6.62	3.67	3.65
3A	0.5000	6.60	3.66	3.65
1B	0.5000	6.25	3.46	3.47
2B	0.5000	6.26	3.48	3.47

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[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

RESEARCHES ON AMINES: ALKYLATIONS WITH DIMETHYLSULPHATE. SYNTHESIS OF DIMETHYLPHENYLETHYLAMINE.

(THIRD PAPER.)

BY TREAT B. JOHNSON AND HERBERT H. GUEST.

Received March 23, 1910.

Contents.—1. Historical. 2. Purpose of Investigation and Discussion of Results. 3. Experimental Part.

1. Historical.

That dialkylsulphates (dimethyl- and diethylsulphates) can be used in place of the corresponding halides for the alkylation of amines has been known for a long time. Dumas and Peligot,[1] in 1835, examined the behavior of dimethylsulphate towards ammonia and observed the formation of methylalcohol and methylammonium sulphate (Sulfomethylan). Strecker[2] repeated this experiment and also investigated the action of diethylsulphate on ammonia. He found that the reactions were not as simple as assumed by Dumas and Peligot and obtained, with diethylsulphate, the ammonium salt of an acid, $C_{16}H_{23}NO_4.4SO_3 + NH_3$ (äthylaminschwefelsäure Ammoniak), from which he prepared ethylamine by decomposition with alkali.

Babo[3] examined the action of dimethylsulphate (Schwefelsaures Methyloxyd) on aniline and showed that it alkylated smoothly giving monomethylaniline. He also observed that quinoline and nicotine reacted with this reagent and diethylsulphate giving crystalline addition products (quaternary compounds?).

The study of the action of these sulphates on amines received no further attention, apparently, until 1880 when a paper by Claesson and Lundvall[4] appeared, in which they describe their behavior towards ammonia and several aliphatic and aromatic bases. They repeated the work of Strecker and observed that diethylsulphate reacted with ammonia giving not only

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[1] *Ann. chim. phys.*, 58, 32.

[2] *Ann.*, **75**, 46.

[3] *J. pr. Chem.*, [1] **72**, 84 (1857); *Chem. Centr.*, 218 (1858).

[4] *Ber.*, **13**, 1700.