

The Qualitative and Quantitative Determination of Nickel and Cobalt

By

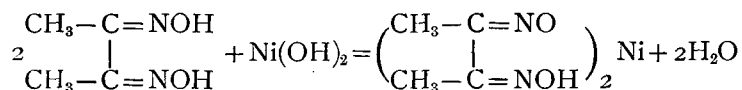
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I. Detection of Nickel

Dimethylglyoxime is now generally used as the most sensitive reagent for nickel which forms an insoluble crystalline precipitate on addition of a 1% alcoholic solution of the reagent. As dimethylglyoxime nickel thus formed is soluble both in strong acids and alkalies, it is necessary to make the nickel solution slightly alkaline with ammonia or to add sodium acetate in an excess beforehand.

Now the reaction between dimethylglyoxime and nickel hydroxide (if such reaction actually takes place) might be expected to proceed quantitatively without the use of ammonia or sodium acetate, as no acid is liberated by the reaction thus:



Moreover, if nickel hydroxide directly changes into dimethylglyoxime nickel, the detection of nickel in a mixture of the hydroxides of the iron group metals will be greatly simplified. With these expectations we have experimented in the reaction between dimethylglyoxime and nickel hydroxide.

Nickel hydroxide prepared from the sulphate, after having been repeatedly washed with water, was mixed with a 1% alcoholic solu-

tion of dimethylglyoxime and well shaken, whereupon a reaction instantly took place, and the nickel was completely changed into the glyoxime compound. Ferric hydroxide was observed to have practically no action upon the glyoxime, while cobalt hydroxide partly changes into the glyoxime compound and dissolves. If, therefore, nickel hydroxide is contaminated with the hydroxides of iron and cobalt, especially when small quantities of the former are mixed with large quantities of other hydroxides, the nickel hydroxide is completely hidden by other hydroxides and escapes detection. This obstacle may, however, be easily overcome in the following way: A mixture is treated with an excess of the dimethylglyoxime solution and boiled for a short time. Water is then added in considerable quantities and the mixture cooled. The solution is now well shaken with ether and left to stand, when dimethylglyoxime nickel floats up with ether, leaving unchanged hydroxides which gradually sink to the bottom of the test-tube.

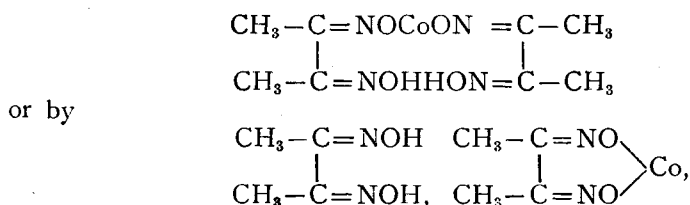
Nickel sulphide also directly changes to dimethylglyoxime nickel, but this action proceeds so slowly, that the quantitative transformation is practically impossible. Glyoxime nickel formed from nickel sulphide may also be separated from the unchanged sulphide by means of ether as described above.

II. Detection of Cobalt

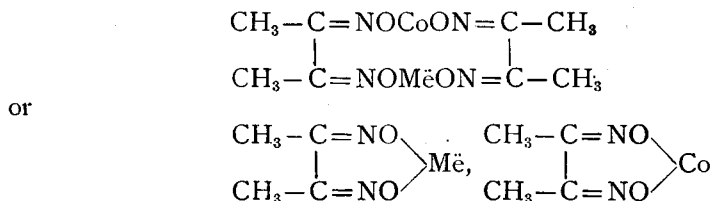
A solution of dimethylglyoxime cobalt is always produced as the filtrate, whenever nickel is separated from cobalt as the glyoxime compound. On endeavouring to find some reaction of the solution which may serve for the detection of cobalt, we found that *when a drop or two of yellow ammonium sulphide is added to it, the solution produces a very intense red colour*. This colour reaction of dimethylglyoxime cobalt is very delicate and does not fail to show the presence of even mere traces of cobalt. High delicacy is attained when a neutral cobalt salt mixed with an excess of a dimethylglyoxime solution is employed. In an ammoniacal solution or in a solution in which an excess of sodium acetate is added, the red colouration is less intense and gradually increases in intensity by standing. It should be remembered that the presence of a large excess of glyoxime is essential, otherwise, cobalt is precipitated as the sulphide. Dimethylglyoxime compound of ferrous iron is also of

a red colour, so that iron should be previously removed from the solution as ferric hydroxide.

Dimethyl glyoxime cobalt is regarded to have the constitution represented either by



and therefore double compounds, such as



may be expected to be derived from it. We have sought some such compound having slight solubility; but so far as our experiments are concerned, all trials ended negatively. The only compound which has been found to have comparatively slight solubility was lead cobalt compound. It is prepared from a glyoxime cobalt solution on addition of lead acetate as orange yellow crystals. It has the tendency to form a supersaturated solution, so that, from its dilute solution the precipitation takes place only after some time, and is hastened by stirring the liquid with a glass rod.

The results of its analysis are as follows:

	Calc.	Found
Pb	41.65	41.92 %

III. Electrolytic determination of Nickel and Cobalt

The methods usually adopted for quantitative determination of nickel and cobalt in their mixture are those of Fischer¹ and of v.

¹ Pogg. Ann. **72**, 477 (1847).

Liebig¹. According to the former, cobalt is first precipitated as potassium cobaltinitrite, while by the latter method nickel is separated from cobalt in the form of an oxide by oxidising the mixed complex cyanide solution. Both methods give a satisfactory result when conducted carefully; still the process is somewhat tedious and requires considerable time.

Since the discovery of dimethylglyoxime as the precipitant of nickel, the separation of the two metals has become very simple, and O. Brunck² has further confirmed the fact, that the reagent may as well be used for the quantitative analysis of nickel. The most convenient method now employed for the quantitative separation and determination of nickel and cobalt is to determine nickel as the dimethylglyoxime [compound on the one hand, and to estimate the total quantities of nickel and cobalt by electrolysis on the other.

Now we have undertaken to see if it is not possible to deposit metallic cobalt quantitatively by electrolysing a dimethyl glyoxime cobalt solution which is obtained as the filtrate whenever nickel is precipitated as the glyoxime compound, and also we have experimented on the electrolytic behaviour of nickel glyoxime.

1. *Electrolysis of Nickel dimethyl glyoxime*

Nickel dimethyl glyoxime was dissolved in a caustic soda solution and electrolysed at the ordinary temperature. When the amount of nickel in the electrolyte was less than 0.05 gram in 100 c.c., an excellent result was obtained; the deposit was of a greyish white colour, contained no trace of carbon, and adhered well to the electrode. Sometimes nickel oxide was observed to be deposited at the anode. In such a case dilute alcohol containing some glycerin (alcohol 45 c.c., glycerin 4 c.c. and water 50 c.c.) was poured into the electrode so as to redissolve it. If the amount of nickel present is more than that above mentioned, or if the temperature of the bath is higher than 50°, the oxide formed at the anode increases and consequently the deposition of metal at the cathode becomes incomplete.

The results of analysis is given in the following table :

¹ Ann. d. Chem. **87**, 128 (1853).

² Zs angew. Chem. **20**, 834, 1844 (1907).

TABLE I

Electrode	Ni		Electrolyte	Vol. (c.c.)	Volt	Amp	Temp.	Hour
	used	found						
Classen's Basin	0.0203	0.0202	8 ^{gr.} NaOH	150	3.2	1.5	18-35°	3.0
„	0.0406	0.0406	9.6 ^{gr.} NaOH	150	3.5	1.5	18-30°	2.5
„	0.0203	0.0199	8 ^{gr.} NaOH	150	2.7	1.5	60-70°	2.0

2. Electrolysis of Cobalt dimethyl glyoxime

The cobalt dimethyl glyoxime solution added with an excess of sodium hydroxide was electrolysed with a result similar to that of the electrolysis of the nickel compound. In this case a much more concentrated solution may be used without fear of the formation of the oxide at the anode ; but once formed, it is more difficult to remove. Temperature of the bath should be kept below 50°.

The results are as follows :

TABLE II

Electrode	Co		Electrolyte	Vol. (c.c.)	Volt	Amp	Temp	Hour
	used	found						
Classen's Basin	0.0278	0.0276	4 ^{gr.} NaOH	100	3.2	0.8	Below 30°	3.0
„	0.0556	0.0555	5.6 ^{gr.} NaOH	100	3.0	0.8	„	3.2
„	0.0218	0.0136	4.8 ^{gr.} NaOH Dimethyl glyoxime not in excess	100	2.5	0.8	60-70°	2.5

By using ammonia instead of sodium hydroxide, the formation of oxide at the anode can, to some extent, be avoided, the results being shown in table IV.

3. Separation of Nickel and Cobalt by Electrolysis of their Dimethyl glyoxime compounds

To a mixed solution of nickel and cobalt sodium acetate was added in an excess, and from this solution nickel was precipitated as the dimethyl glyoxime compound. The precipitate was filtered, and

after having been well washed warmed on a waterbath with a suitable amount of sodium hydroxide. The alkaline solution of dimethyl glyoxime nickel thus obtained was electrolysed. The filtrate containing cobalt was added, with sodium hydroxide, or with ammonia and ammonium sulphate, and was subjected to electrolysis.

The results are shown in the following table :

TABLE III

Electrode	Metal		Electrolyte	Vol. (c.c.)	Volt	Amp	Temp.	Hour
	used	found						
Platinum Net	Ni, 0.0450	0.0448	8 ^{gr.} NaOH	100	2.5	1.0	Room temp.	2.5
	Co, 0.0015	0.0014	3.2 ^{gr.} „		3.2			1.0
Classen's Basin	Ni, 0.0360	0.0361	6.4 ^{gr.} NaOH	100	2.5	1.0	„	„
	Co, 0.0015	0.0014	2.4 ^{gr.} NaOH		3.0			„
„	Ni, 0.0153	0.0154	4.8 ^{gr.} NaOH	100	2.3	1.0	„	1.5
	Co, 0.0015	0.0014	2.0 ^{gr.} NaOH		2.8			1.0

TABLE IV

Electrode	Metal		Electrolyte	Vol. (c.c.)	Volt	Amp	Temp	Hour
	used	found						
Net	Ni, 0.0542	0.0540	8 ^{gr.} NaOH	100	2.5	1.0	Room temp.	2.5
	Co, 0.0306	0.0305	60 c.c. NH ₄ OH 2.6 ^{gr.} (NH ₄) ₂ SO ₄		3.6			2.3
„	Ni, 0.0067	0.0065	4.8 ^{gr.} NaOH	100	3.0	0.8	„	1.7
	Co, 0.1836	0.1835	40 c.c. NH ₄ OH 5 ^{gr.} (NH ₄) ₂ SO ₄		4.1			3.5
„	Ni, 0.0102	0.0100	4.8 ^{gr.} NaOH	100	3.2	1.0	„	2.5
	Co, 0.1836	0.1834	50 c.c. NH ₄ OH 2 ^{gr.} (NH ₄) ₂ SO ₄		3.8			3.3

4. *Rapid Precipitation*

By agitating the electrolyte, the deposition of metal is of course accelerated, but as it is necessary to regulate the current density so as to keep the temperature of the bath below 50° no remarkable acceleration could thus be affected.

TABLE V

Metal	Electrolyte	Vol. (c.c.)	Volt	Amp	Temp	Hour	Deposit
Ni=0.0241	0.1 ^{gr.} glyoxime 4.8 ^{gr.} NaOH	100	4	4.5	Below 4.5	0.8	0.0239
Co=0.0612	0.2 ^{gr.} glyoxime 4.8 ^{gr.} NaOH	"	"	2	"	1.2	0.0610

5. *Conclusion*

As the conclusion of the above experiment the following methods of the electrolysis of dimethyl glyoxime nickel and cobalt are deduced.

TABLE VI

Metal	Electrolyte	Vol. (c.c.)	Volt	Amp	Temp.	Hour
Ni or Co 0.01-0.05	0.2 ^{gr.} dimethyl glyoxime 4.8 ^{gr.} NaOH	100	2.5- 3.0	1.0	Below 50°	1-3

TABLE VII (Rapid method)

Metal	Electrolyte	Vol. (c.c.)	Volt	Amp	Temp.	Minutes	No. of rotation
Ni 0.02- 0.05	0.2 ^{gr.} dimethyl glyoxime 5.5 ^{gr.} NaOH	100	3.8- 4.0	3.5	Below 50°	50	800
Co "	0.2 ^{gr.} dimethyl glyoxime 6.5 ^{gr.} NaOH	"	4.0- 4.5	"	"	"	"