## OXALENEDIAMIDOXIME. PART I. ESTIMATION OF NICKEL.

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Oxalenediamidoxime has been used as an analytical reagent for the estimation of nickel up to 0°006 g., and for its separation from zinc and manganese. Quantitative separation from cobalt has been found possible within narrow limits of concentrations of cobalt.

It is well known that the atomic grouping HON=C-C=NOH reacts specifically with the nickel ion in a characteristic fashion to form inner metallic complexes of the type

The monobasicity of dioximes obviously lowers the percentage content of nickel in the complex, and the simultaneous saturation of primary and co-ordination valences by chelation lowers the solubility of such complexes in highly polar solvents like water, both of which effects are favourable for the utilisation of such organic molecules as analytical reagents.

It may be pointed out that the best known compound among this class of dioximes, viz., dimethylglyoxime, has the disadvantage of not being quite soluble in aqueous media from which nickel is precipitated, and that the complex itself has fair solubilities in both acids and ammonia. A similar dioxime possessing, however, greater solubility in water, has been found in oxalenediamidoxime, and the possibility of using this as a precipitant for nickel has been indicated here. It may be seen from the results obtained that, leaving perhaps the important application of dimethylglyoxime as a reagent for the separation of nickel from cobalt, this diaminodioxime serves quite a satisfactory reagent for the individual estimation of nickel, and in its separation from other metals of group IIIB of the analytical table. The slow, incomplete precipitation of cobalt is doubtless connected with the amine character of the reagent (Feigl and Christiani-Kronwald, Z. anal. Chem., 1925, 68, 341), but the dark brown, powdery compound appears to the present author to be more complex than the simple cobalt analogue of the nickel dioxime compound.

The constitutional formula of the nickel complex is tentatively given as

$$\begin{array}{c|c}
OH \\
NH_2 \cdot C = NO \\
NH_2 \cdot C = N
\end{array}$$

$$\begin{array}{c|c}
OH \\
N = C \cdot NH_2 \\
ON = C \cdot NH_2
\end{array}$$

$$OH$$

$$ON = C \cdot NH_2$$

in analogy with the dimethylglyoxime complex.

## EXPERIMENTAL.

Preparation of the Reagent.—Fischer's method of preparation was followed (Ber., 1889, 22, 3930). A rapid stream of cyanogen gas was passed into a concentrated, ice-cold, aqueous solution of hydroxylamine hydrochloride (1 mol.) and caustic potash (1 mol.). Oxalenediamidoxime separated in colourless crystals, and was purified by recrystallisation from hot water (m.p. lit. 200° with decomp., found, 199° with decomposition). The reagent is readily soluble in hot water; a dilute solution of the reagent was used in the estimations.

Nickel Oxalenediamidoxime.—The light orange, crystalline precipitate of the nickel complex, obtained by precipitating with a dilute solution of the reagent from faintly ammoniacal solution of nickel chloride containing ammonium chloride, was washed with cold water, and readily obtained anhydrous by drying at 110-120° for half an hour. [Found: Ni. (by ignition to oxide), 20'02. Calc. for Ni(C<sub>2</sub>H<sub>3</sub>N<sub>4</sub>O<sub>2</sub>)<sub>2</sub>: Ni, 20'04 per cent].

Estimation of Nickel.—A solution of chemically pure nickel chloride containing about o'2% nickel was prepared and standardised by the dimethylglyoxime method. Certified standard pipettes were used for measuring out known volumes of nickel solution. To the nickel solution at room temperature was added a cold dilute solution of the reagent in slight excess, and then ammonium hydroxide drop by drop with stirring, till the solution smells of ammonia. The light orange precipitate of the nickel complex was allowed to settle, filtered through asbestos filter, washed with cold water, dried at 110-120°, and weighed. Table I shows the results.

TABLE I.

Wt. of Ni oxime ppt.	Weight of found.	fnickel taken.	Wt. of Ni oxime ppt.	Weight of found.	nickel taken.
0.0297 g. 0.0596	o'00595 g. o'01194	0.00598 g. 0.01195	0.1130 0.111 <b>0</b> B	0°0224 g. 0°0224	0°0224 g. 0°0224
0.1163	0.0538	0.0530	0.1111	0.0553	0.0154

Separation of Nickel from Zinc and Manganese.—A known volume of the standard nickel solution was mixed respectively with known volumes of zinc and manganous chloride solutions, containing approximately known amounts of Zn and Mn. The mixture was in each case treated with a sufficient quantity of ammonium chloride to prevent precipitation of the hydroxides in ammoniacal medium. Nickel was then precipitated and estimated as described above. The results are shown in Table II.

TABLE II.

Composition of soln.		Wt. of ppt.	Wt. of Ni found.	Error.
		0'1112 g.		
0'0239	0.022	0.1130	0-0238	-0'0001
0.0230	0.02	0.1163	0.0530	NiI
0-0239	0'125	0.1136	0'0240	+*0001
0.0536	0.22	0"1192	0.0536	Nil
0.0530	0.372	0,1101	0.0530	Nil
0.0224	0.014 Ми	0.1112	0.0224	Nil
0.0339	0.054	0.1104	0.0239	หก
0.0239	0.048	0.1100	0.0340	+0,0001
0.0530	0.24	0.1100	0.0240	+0.0001
0.0539	0.36	0.1163	0.0239	Nil

Separation of Nickel from Cobalt.—A dark brown, insoluble powder slowly separated from ammoniacal solutions containing cobalt on the addition of the reagent. The precipitation was found to be accelerated by passing a current of air, and temporarily prevented by the addition of hydroxyllamine hydrochloride. The estimation of nickel in presence of cobalt was carried out in exactly the same manner as in other cases, with the only difference that nearly I g. of hydroxylamine hydrochloride was added for every 100 c.c. of the solution, before rendering the sclution ammoniacal. Some of the results are shown in the following table. Larger amounts of cobalt than those shown here led to high results for nickel.

TABLE III.

Composition of soln.		Wt. of ppt.	Wt. of Ni found. 0°0240 g.	Error. +0-0001
		o·1199 g.		
0.0538	0.025	0.1180	0-0238	-0.0001
0.0330	0.02	0.1163	0.0536	Nil

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