

## DETECTION OF NICKEL IN COBALT SALTS.

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The use of dimethylglyoxime as a reagent for the detection and determination of nickel, discovered by Tschugaev<sup>1</sup> in 1905 and developed by Brunk,<sup>2</sup> has become a general practice. For simplicity of manipulation and freedom from interference this reagent is unrivalled; the brilliant scarlet color and extreme insolubility of the nickel glyoximine renders possible the detection of one part of nickel ion in at least 350,000 parts of water. By a modified method of applying the reagent, which was developed in the course of this investigation, we found it possible to detect one part of nickel ion in more than 4,000,000 parts of water.

For detection of traces of nickel in cobalt salts this reagent, hitherto, has not been very satisfactory. Cobalt combines with dimethylglyoxime to form an extremely soluble compound of brown color. Either because the nickel salt is soluble in this compound, or, as is much more probable, because the cobalt appropriates most of the reagent, no nickel is precipitated by ordinary amounts of reagent from cobalt salt solutions, even though a considerable amount is present. The object of this investigation was to devise a method by which the cobalt ion should be suppressed, thus permitting the reagent to react with nickel only thus avoiding the necessity for large amounts of reagent. Treadwell,<sup>3</sup> following a suggestion of Tschugaev, accomplishes this result by transforming the cobalt salt into a cobaltic ammin by strong ammonia and hydrogen peroxide before adding dimethylglyoxime. We shall show that this method is unsatisfactory and fails when much cobalt is present.

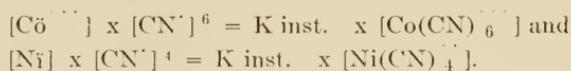
The most striking differences in the chemical behavior of nickel and cobalt are (1) the greater readiness of oxidation to the trivalent condition and (2) the greater stability of the complex ions, both positive and negative, of cobalt. Of the various complex ions formed by cobalt the most stable are the complex cyanides, that of trivalent cobalt being decidedly more stable than that of bivalent cobalt. Nickel forms soluble complex cyanides of a

<sup>1</sup>Ber. 38, 2520.

<sup>2</sup>Z. angew. Chem., 20, 3444.

<sup>3</sup>Analyt. Chem., Vol. I. 151. (7te Aufl.)

different type, resembling those of bivalent copper, whereas the cobalt cyanides are analogous to the iron cyanides. In the classic method of Liebig<sup>4</sup> for detecting nickel in cobalt salts, the inferior stability of nickelocyanide ion together with the ready oxidizability of cobaltocyanide to cobalticyanide ion has long been used to effect a separation. For a solution containing cobalticyanide, nickelocyanide and cyanide ions the following equilibria are involved:



The values of the instability constants are not accurately known, but it is certain that that of cobalticyanide ion is extremely small and that of nickelocyanide ion much larger. Any reduction of the concentration of cyanide ion in the solution must result in decomposition of the nickelocyanide ion and considerable increase of nickel ion concentration while the much more stable cobalticyanide ion is less affected. In Liebig's method as modified by Gauhe,<sup>5</sup> cyanide ion is removed by oxidation with alkaline hypobromite or hypochlorite, the nickelous ion being simultaneously oxidized and precipitated as  $\text{Ni}(\text{OH})_3$ . This method is not altogether satisfactory, first, because, owing to the necessity of adding an excess of the oxidizing agent, cobaltic hydroxide is also precipitated invariably so that the appearance of a brown precipitate is not *per se*, proof of the presence of nickel; second, because the manipulation, particularly the amounts of reagents, requires experience and care.

Nickel glyoximine is decomposed by cyanide ion. Our problem, then, was to remove the cyanide ion so gradually that the cobalticyanide ion should remain practically unaffected. For this purpose we made use of the great stability of complex silver cyanide ions, together with the high insolubility of silver argenticyanide,  $\text{Ag} \cdot \text{Ag}(\text{CN})_2$ , 0.0004 g. per liter<sup>6</sup> at 20°. For argenticyanide ion,  $[\text{Ag}] \times [\text{CN}]^2 = 10^{-21} \times [\text{Ag}(\text{CN})_2^{-}]$ . The comparative insolubility of silver cobalticyanide,  $\text{Ag}_3\text{Co}(\text{CN})_6$ , accurate data for which are lacking, should also tend to prevent decomposition of cobalticyanide ion. When dimethylglyoxime is added to very dilute solutions of nickel salts,

<sup>4</sup>Ann., 65, 244 (1848); 87, 128 (1853).

<sup>5</sup>Z. analyt. Chem., 5, 75 (1866).

<sup>6</sup>Brodig, Z. physik. Chem., 46, 602.

a yellow color at once develops and the red precipitate flocculates after a brief interval. At extreme dilutions where no precipitate forms, a yellow tint is observable. This was suspected to be due to colloidal glyoximine which should be flocculated by another precipitate, in which case, since both silver cyanide and silver cobalticyanide are white, the red nickel glyoximine would be readily detectable and the delicacy of the test increased. The correctness of this view seems to be confirmed by the experimental results detailed below.

#### EXPERIMENTAL.

**Solutions and Reagents.**  $\text{NiSO}_4$  solution, approx. 0.05 molar, from Kahlbaum's "Kobalt-frei" salt, was standardized by electrolysis (0.05008 molar) and by precipitation and weighing as nickel glyoximine (0.0496 molar). The discrepancy is due probably to a trace of iron which was detected, the removal of which appeared unnecessary for our purpose. The more dilute solutions used were prepared from this by accurate dilution.

7) Bodlander, Z. anorg. Chem, 39, 227.

$\text{CoSO}_4$ , approx. 0.1 molar, was prepared by working up residues from cobaltammin salts. Nickel was removed by dimethylglyoxime according to the method we have developed and the solution as used gave no evidence of nickel by any of the tests applied. Electrolysis showed this solution to be 0.0921 molar. Potassium cyanide, 10 per cent. solution. Dimethylglyoxime, 1 per cent. solution in alcohol. Silver nitrate, 1 per cent. solution.

#### SENSITIVENESS OF DIMETHYLGLYOXIME AS A REAGENT FOR NICKEL IN PRESENCE AND IN ABSENCE OF CYANIDE ION.

Ten cc. of  $\text{NiSO}_4$  solution of molarity stated in the table below was warmed to about  $80^\circ$  and 1 cc. of the reagent added and a drop or two of dilute ammonia. To the same volume of each  $\text{NiSO}_4$  solution two or three drops of KCN were added. At these high dilutions no precipitate was formed. The solution was warmed to  $80^\circ$ , 1 cc. of reagent added and then the  $\text{AgNO}_3$  solution dropwise until a permanent white or pink precipitate formed. The more concentrated solutions gave at once a pink precipitate; the more dilute ones a white precipitate which turned pink on standing. In those solutions which required more than one hour to form a precipitate the exact

time required for the pink precipitate to appear was not recorded. The samples were observed after standing 24 hours. From the results tabulated below it is apparent that the test is at least as delicate in the presence as in the absence of cyanide and that the results are obtainable much more quickly from the complex than from the simple ion. In the extreme dilutions of the simple ion the precipitate was frequently a single red crystal very minute and difficult to see.

TABLE I.

Molarity.	TIME.		Mg. Ni per cc.	Ratio Ni : H <sub>2</sub> O
	NiSO <sub>4</sub>	K <sub>2</sub> Ni(CN) <sub>4</sub>		
0.0005	Immediate	Immediate	0.02934	1 : 34,000
00005	1 hour	3 min.	002934	1 : 340,000
00001	24 hours	5 min.	000587	1 : 1,700,000
.000009	24 hours	10 min.	000528	1 : 1,900,000
000008	24 hours	20 min.	000470	1 : 2,130,000
000007	24 hours	30 min.	000411	1 : 2,430,000
000006	24 hours	1 hour	000352	1 : 2,840,000
000005	24 hours	21 hours	000293	1 : 3,400,000
000004	No ppt.	24 hours	000235	1 : 4,260,000
000003	No ppt.	No pink color	.000176	1 : 5,700,000
000002	No ppt.	No pink color	.000117	

### 3. OXIDATION OF COBALTCYANIDE ION TO COBALTCYANIDE ION.

When KCN is added to a solution of cobalt salt, brown-red  $\text{Co}(\text{CN})_2$  is first precipitated and then redissolved to a brown solution of  $\text{K}_4\text{Co}(\text{CN})_6$ . On heating this soon changes to a pale yellow and the color change is generally assumed in manuals of analysis to indicate the completion of oxidation to cobalticyanide. We at first proceeded upon this assumption, but when the first drops of  $\text{AgNO}_3$  were added to some of our complex cyanide solutions, soon after the color change took place, the solution darkened and addition of more  $\text{AgNO}_3$  produced a dark-gray precipitate while solutions which had stood for several hours did not darken and gave a pure white precipitate. When one of the darkened solutions became distinctly opalescent, we suspected that colloidal silver had been formed. This was explainable by the assumption that  $\text{AgNO}_3$  had been reduced by cobalticyanide which was still present according to  $\text{K}_4\text{Co}(\text{CN})_6 + \text{AgNO}_3 = \text{K}_3\text{Co}(\text{CN})_6 + \text{Ag} + \text{KNO}_3$ .

By adding  $\text{AgNO}_3$  to freshly prepared solutions of cobaltocyanide we found that this reaction takes place very slowly in cold but rapidly in hot solutions. When the  $\text{AgNO}_3$  was added dropwise, the hot solutions first became lighter in color, then gradually turned orange and darkened until a gray precipitate was formed. If the addition of  $\text{AgNO}_3$  was stopped when the orange tint appeared, no precipitate formed, but the solution darkened on standing and became opalescent, showing that colloidal silver had formed. We found that this phenomenon was regularly reproducible in solutions of cobaltocyanide not less than 0.005 molar. These experiments clearly show that the oxidation of cobaltocyanide is by no means complete when the color change takes place. We next investigated the time required to complete the oxidation, taking the failure to form metallic silver as evidence that the oxidation was essentially complete.

10 cc. of 0.1 molar  $\text{CoSO}_4$  solution was treated in a casserole with just enough  $\text{KCN}$  to dissolve the  $\text{Co}(\text{CN})_2$ , the solution heated nearly to boiling and continuously rotated in the casserole for a definite time to promote oxidation. The solution was then diluted to 100 cc. with water at  $85^\circ$  and  $\text{AgNO}_3$  added dropwise with vigorous stirring. Results are given below.

TABLE II.

Cc. 0.1 molar $\text{CoSO}_4$	Time Heated.	Result.
10.....	2 min.....	Colloidal Ag.
10.....	3 min.....	Orange soln.; gray ppt.
10.....	4 min.....	Orange soln.; gray ppt.
10.....	5 min.....	No darkening of soln.; ppt. white.

These results show that heating with constant agitation must be continued for some time after the change of color. Presumably the time required increases with the amount of cobalt present.

#### DETECTION OF NICKEL IN COBALT SALTS.

We next determined the minimum amount of nickel that could be detected in varying amounts of cobalt by our silver method and, for comparison, by Treadwell's and the modified Liebig.

## A. THE SILVER METHOD.

Definite volumes of solutions of  $\text{NiSO}_4$  and  $\text{CoSO}_4$  of known concentration were measured from burets into a casserole, KCN added until the precipitate just dissolved, and the solution heated and rotated until complete oxidation was effected. The solution was then diluted with water at  $85^\circ$  to 50 cc., 1 cc. of dimethylglyoxime solution added, and then  $\text{AgNO}_3$  dropwise with vigorous stirring until a permanent precipitate was produced. The time required for the pink color of nickel glyoximine to appear was observed. In cases where the time exceeded one hour, observations were made at the end of 24 hours. The results are given below.

TABLE IV.

In each expt. 10 cc.  $\text{CoSO}_4$  0.0921 molar, equivalent to 54.31 mg. Co, was used.

$\text{NiSO}_4$		Mg. Ni.	Ratio Ni : Co.	Ratio Ni : $\text{H}_2\text{O}$	Results.
Vol.	Conc. molar				
2 cc.	0.0005	0.0587	1 : 925	1 : 852,000	Ppt. pink immediate.
1.5 cc.	0.0005	.0440	1 : 1234	1 : 1,140,000	Ppt. pink 4 min.
1.0 cc.	0.0005	.0293	1 : 1851	1 : 1,707,000	Ppt. pink 6 min.
4.5 cc.	.0001	.0264	1 : 2054	1 : 1,894,000	Ppt. pink 10 min.
4.0 cc.	.0001	.0235	1 : 2314		Ppt. pink 20 min.
3.5 cc.	.0001	.0205	1 : 2644	1 : 2,440,000	Ppt. pink 30 min.
3.0 cc.	.0001	.0176	1 : 3085		Ppt. pink 24 hours.
2.5 cc.	.0001	.0137	1 : 3702	1 : 3,650,000	Ppt. pink 24 hours.

Taking the minimum amount of nickel that could be detected in cobalt in 30 minutes, 0.0205 mg., we observed the effect of larger proportions of cobalt. The procedure and final total volume of solution were the same as in the preceding experiments.

TABLE V.

$\text{CoSO}_4$ 0.0921 molar	Mg. Co.	Ratio Ni : Co	Results.
15 cc.	81.47	1 : 3966	Ppt. pink 30 min.
20 cc.	108.62	1 : 5288	Ppt. pink 30 min.
25 cc.	135.78	1 : 6610	Ppt. pink 30 min.
30 cc.	162.93	1 : 7932	Ppt. pink 30 min.

These results show that the sensitiveness of the test is not impaired by the presence of large amounts of cobalt.

#### B. THE TSCHUGAEV-TREADWELL METHOD.

10 cc. portions of 0.0921 molar  $\text{CoSO}_4$ , equivalent to 54.31 mg. Co., with varying small amounts of  $\text{NiSO}_4$  were heated with ammonia until a clear solution was obtained, hydrogen peroxide added and the solutions heated till excess of peroxide and ammonia was removed, diluted to 50 cc., 1 cc. of dimethylglyoxime solution added and the time required for the red precipitate to appear was observed. Results below.

TABLE VI.

$\text{NiSO}_4$		Mg. Ni.	Ratio Ni : Co.	Results.
Vol.	Conc. molar			
10 cc.....	0.0005	0.2934	1 : 185	Red ppt. 1 hour.
9 cc.....	0.0005	.2641	1 : 206	Red ppt. 1 hour.
8 cc.....	0.0005	.2347	1 : 231	Red ppt. 1 hour.
7 cc.....	0.0005	.2052	1 : 264	Red ppt. 24 hours.
6 cc.....	0.0005	.1760	1 : 309	Red ppt. 24 hours.
5 cc.....	0.0005	.1467	1 : 370	Red ppt. 24 hours.
4 cc.....	0.0005	.1172	1 : 462	Red ppt. 24 hours.

Taking the minimum amount of nickel that could be detected in 1 hour, 0.2347 mg., we observed the effect of larger proportions of cobalt. The procedure and final volume were the same as in the experiments recorded in Table VI.

TABLE VII.

$\text{CoSO}_4$ 0.0921 molar	Mg. Co	Ratio Ni : Co	Results.
10 cc.....	54.31	1 : 231	Red ppt. after 1 hr.
15 cc.....	81.47	1 : 346	No ppt. after 1 hr.
20 cc.....	108.62	1 : 462	No ppt. after 1 hr.
25 cc.....	135.78	1 : 577	No ppt. after 1 hr.
30 cc.....	162.93	1 : 693	No ppt. after 1 hr.

These results indicate that this method is not very sensitive and fails when much cobalt is present.

### C. THE LIEBIG-GAUHE METHOD.

10 cc. portions of  $\text{CoSO}_4$ , 0.0921 molar, with varying amounts of  $\text{NiSO}_4$  were treated with a slight excess of KCN over that required to dissolve the precipitate, and heated and rotated until complete oxidation of the cobaltocyanide had taken place. They were then diluted to 50 cc. and freshly prepared sodium hypobromite added. After the precipitate had flocculated, it was filtered off, washed, dissolved in dilute HCl, neutralized with ammonia and tested for Ni with dimethylglyoxime. Results below.

TABLE VIII.

$\text{NiSO}_4$ 0.005 molar	Mg. Ni.	Ratio Ni : Co	Ratio Ni : $\text{H}_2\text{O}$	Results.
9 cc.....	0.2641	1 : 206		Blk. ppt. Ni confirmed
6 cc.....	.1760	1 : 309		Blk. ppt. Ni confirmed
4 cc.....	.1172	1 : 462		Blk. ppt. Ni confirmed
3 cc.....	.0880	1 : 617	1 : 568,000	Blk. ppt. Ni confirmed
2 cc.....	.0587	1 : 925	1 : 852,000	Blk. ppt. No Ni
1 cc.....	.0293	1 : 1850		Blk. ppt. No Ni
None.....	None			Blk. ppt. No Ni

This method is shown to be capable of detecting 0.1 mg. nickel in a volume of 50 cc., but a confirmatory test must in every case be applied as the ppt. contains  $\text{Co(OH)}_3$ .

Comparing the results of the three methods, the minimum amount of nickel detectable within one hour in a volume of 50 cc. is found to be:

Silver .....	0.02 mg.
Tschugayev-Treadwell.....	.23 mg.
Liebig-Gauhe.....	.09 mg.

These figures do not adequately convey the relative merits of the three methods, for it should be noted in addition that the Liebig method requires a confirmatory test to make the result trustworthy; the Treadwell method failed to show the stated minimum amount of nickel when so little as 231 times as much cobalt as nickel was present, while the silver method appears

to retain its full sensitiveness in presence of any amount of cobalt; and that it has been shown to increase the effectiveness of dimethylglyoxime about eight times and to be able to detect within 24 hours less than 0.002 mg. of nickel in a volume of 50 cc.

#### SUMMARY.

1. A modified method of using dimethylglyoxime for detecting traces of nickel in cobalt salts is proposed which (1) avoids the use of large amounts of the reagent; (2) makes possible the detection of considerably smaller quantities of nickel than has been possible heretofore.

2. The sensitiveness of the test is shown to be unaffected by the presence of cobalt even in large quantities. The proposed method increases the ordinary sensitiveness of dimethylglyoxime about eight times and is capable of detecting about one-fifth the amount of nickel detectable by any of the previously known methods.

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