[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY.]

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[1] in 1905 and developed by Brunk,[2] has become quite general. In addition to its simplicity of manipulation and freedom from interference by other metallic ions this reagent is unusually delicate. The brilliant scarlet color and extreme insolubility of nickel glyoximine[3] permits detection of one part of nickel in at least 350,000 parts of water and a modified method of using the reagent will be described in this paper by which we have been able to detect one part of nickel in more than 4,000,000 parts of water.

For the detection of traces of nickel in cobalt salts this reagent has not proved entirely satisfactory.[4] Cobalt combines with dimethylglyoxime to form an extremely soluble compound of brown color. Either because the nickel salt is soluble in this compound or, more probably, 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 and avoiding the necessity for large amounts of reagent. Treadwell,[5] following a suggestion of Tschugaev, accomplishes this result by transforming the cobalt salt into a cobaltic ammine by concentrated 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 susceptibility of the latter to oxidation to the trivalent condition, and (2) the greater stability of its complex ions, both positive and negative. 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 complex cyanides of a different type, resembling those of bivalent copper, whereas the cobalt cyanides are analogous to the iron cyanides. In the classic method of Liebig[6] for detecting nickel in cobalt salts, the inferior stability of the nickelocyanide ion together with the ready oxidizability of cobaltocyanide to cobalticyanide has long been used to effect a separation. For

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[1] *Ber.*, 38, 2520 (1905).

[2] *Z. angew. Chem.*, 20, 3444 (1907).

[3] The nomenclature of Tschugaev, *Z. anorg. Chem.*, 46, 147 (1905).

[4] Cf. E. F. Smith, *Trans. Am. Electrochem. Soc.*, 27, 31 (1915).

[5] *Analyt. Chem.*, 1, 151, 7th ed.

[6] *Ann.*, 65, 244 (1848); 87, 128 (1853).

a solution containing cobalticyanide, nickelocyanide and cyanide ions the following equilibria are involved:

$$[\mathrm{Co}'''] \times [\mathrm{CN}^{\cdot}]^6 = \mathrm{K}_{\mathrm{inst.}} \times [\mathrm{Co(CN)}_6^{\cdot\cdot\cdot}] \quad \text{and}$$

$$[\mathrm{Ni}''] \times [\mathrm{CN}^{\cdot}]^4 = \mathrm{K}_{\mathrm{inst.}} \times [\mathrm{Ni(CN)}_4^{\cdot\cdot}]$$

The values of the instability constants are not accurately known, but it is certain that that of the cobalticyanide ion is extremely small and that of the nickelocyanide ion much larger. Any reduction of the concentration of the 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[1] the cyanide ion is removed by oxidation with alkaline hypochlorite or hypobromite, the nickelous ion being simultaneously oxidized and precipitated as nickelic hydroxide. This method is not altogether satisfactory because cobaltic hydroxide is usually precipitated also and the appearance of a brown precipitate is by no means certain proof of the presence of nickel.

Since nickel glyoximine is decomposed by the cyanide ion, our problem was to remove the cyanide ion so gradually that the cobalticyanide ion should remain practically unaffected. For this purpose we have made use of the great stability of complex silver cyanide ions, together with the small solubility of silver argenticyanide, $\mathrm{Ag[Ag(CN)_2]}$, 0.0004 g. per liter at 20°.[2] For argenticyanide ion, $[\mathrm{Ag}'] \times [\mathrm{CN}^{\cdot}]^2 = 10^{-21} \times [\mathrm{Ag(CN)}_2^{\cdot}]$.[3] The comparative insolubility of silver cobalticyanide, accurate data for which are lacking, should also tend to prevent decomposition of the cobalticyanide ion. If to a solution containing alkali salts of nickelocyanide, cobalticyanide and a small excess only of cyanide, dimethylglyoxime be added and then dilute silver nitrate solution gradually, precipitation of silver argenticyanide removes the cyanide ion and promotes decomposition of the nickelocyanide ion, increasing the concentration of the nickelous ion, while the cobalticyanide ion is precipitated as $\mathrm{Ag_3Co(CN)_6}$, or, if not precipitated, is but slightly decomposed. Comparatively little dimethylglyoxime should then be sufficient to precipitate the small amount of nickel present, in part at least. The experiments recorded below show that this modification yields very satisfactory results.

Experimental.

Solutions and Reagents.—Nickel sulfate solution from Kahlbaum's "Kobalt-frei" salt was standardized by electrolysis (0.05008 *N* and by precipitation and weighing as glyoximine 0.04968 *M*). Cobalt, if present, was in very small amount; we were unable to detect it with absolute certainty. Iron was found present and the discrepancy in the electrolytic

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[1] *Z. analyt. Chem.*, 5, 75 (1866).

[2] Bredig, *Z. physik. Chem.*, 46, 602 (1903).

[3] Bodländer, *Z. anorg. Chem.*, 39, 227 (1904).

and precipitation values is probably due almost entirely to its presence. Its removal appeared unnecessary for our purpose. The more dilute solutions used in the work were prepared from this solution by accurate dilution.

Cobalt sulfate solution, approximately 0.1 *M*, was prepared by working up residues from cobalt ammine salts. Nickel was removed by dimethylglyoxime according to the method we have developed and the solution as used gave no test for nickel. By electrolysis this solution was found to be 0.0921 *M*.

The other reagents used were: potassium cyanide, 10% solution; dimethylglyoxime, 1% solution in alcohol; and silver nitrate 1% solution.

Sensitiveness of Dimethylglyoxime as Reagent for Nickel in Absence and in Presence of Silver Cyanide.—Two 10 cc. portions of each of the $NiSO_4$ solutions of the concentrations stated in Table I were taken. One was warmed to about 80°, 1 cc. of the dimethylglyoxime reagent added and a drop or two of dilute ammonia. The other portion was converted into the complex cyanide by adding two or three drops of KCN. At these small concentrations no precipitate of nickel cyanide was formed. The solution was warmed to 80°, 1 cc. of dimethylglyoxime reagent added, and then $AgNO_3$ solution dropwise until a permanent white or pink precipitate formed. The more concentrated solutions thus treated gave at once pink precipitates; the more dilute ones white precipitates 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 color to appear was not recorded. In these cases the samples were observed after standing 24 hours. In the extreme dilutions of the simple ion the precipitate was frequently a single red crystal, very minute and difficult to see.

TABLE I.

Molar conc.	$NiSO_4$.	$K_2Ni(CN)_4$.	Mg. Ni per cc.	Dilution.
0.0005	Immediate	Immediate	0.02934	$1:0.034 \times 10^6$
0.00005	1 hr.	3 min.	0.002934	$1:0.34 \times 10^6$
0.00001	24 hr.	5 min.	0.000587	$1:1.7 \times 10^6$
0.000009	24 hr.	10 min.	0.000528	$1:1.9 \times 10^6$
0.000008	24 hr.	20 min.	0.000470	$1:2.13 \times 10^6$
0.000007	24 hr.	30 min.	0.000411	$1:2.43 \times 10^6$
0.000006	24 hr.	1 hr.	0.000352	$1:2.84 \times 10^6$
0.000005	24 hr.	24 hr.	0.000293	$1:3.4 \times 10^6$
0.000004	No ppt.	24 hr.	0.000235	$1:4.26 \times 10^6$
0.000003	No ppt.	No pink color	0.000176	$1:5.3 \times 10^6$
0.000002	No ppt.	No pink color	0.000117	

From the results tabulated above it appears that the proposed modification shortens considerably the time required for the precipitate of nickel glyoximine to become visible and also makes possible the detection of somewhat smaller concentrations of the nickel ion. Apparently this is due to increased concentration of these ions by adsorption upon the precipitated silver cyanide. As evidence in favor of this view it may be noted that we found that precipitation of silver chloride in extremely dilute solutions of the nickel ion and dimethylglyoxime was equally effective in hastening formation of the pink nickel glyoximine, while precipitation of a positive colloid, such as aluminium hydroxide, had no effect whatever. Since both silver cyanide and silver cobalticyanide are white, the red nickel glyoximine is readily seen as a pink tint in the white precipitate and the delicacy of the reagent is increased.

Oxidation of Cobaltocyanide to Cobalticyanide.—When KCN is added to a solution of a cobalt salt, brownish white $Co(CN)_2$ is precipitated and then redissolved to a greenish brown solution of $K_4Co(CN)_6$. When warmed this changes soon to a pale yellow color and the color change is frequently assumed in manuals of analysis to indicate completion of oxidation. When $AgNO_3$ was added soon after the color change took place, we found that the solutions darkened and dark gray precipitates were formed, while solutions which had stood for several hours after cyanide was added did not darken and gave pure white precipitates. When one of the darkened solutions became distinctly opalescent, we inferred that some silver ion had been reduced by cobaltocyanide which was still present, according to the reaction

$$K_4Co(CN)_6 + AgNO_3 = K_3Co(CN)_6 + Ag + KNO_3.$$

By adding silver nitrate solution to freshly prepared solutions of cobaltocyanide we found that this reaction takes place very slowly in cold but rapidly in hot solutions. When the silver nitrate 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 silver nitrate was stopped when the orange tint appeared, no precipitate formed, but the solution darkened on standing and became opalescent due to the formation of colloidal silver. This reaction was found to be regularly reproducible in solutions of cobaltocyanide not less than 0.005 *M*.

We next investigated the time required after the color change to complete the oxidation, taking the failure to form metallic silver as evidence that oxidation was essentially complete. Ten cc. portions of 0.1 *M* $CoSO_4$ were treated in casseroles with just enough KCN to dissolve the precipitates, heated nearly to boiling and continuously rotated in the casseroles for a definite time to hasten oxidation. The solutions were diluted to 100 cc. with water at 85° and silver nitrate was added dropwise with vigorous stirring. All solutions which had been warmed less than five minutes gave colloidal silver or dark precipitates; those heated for at least this period did not darken and gave pure white precipitates. Presumably the time required increases with the amount of cobalt. Gauhe[1] showed

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[1] *Loc. cit.*

that the oxidation of cobaltocyanide requires considerable time, but his experiments appear to have been forgotten.

Detection of Nickel in Cobalt Salts.—We next determined the minimum amount of nickel that could be detected in varying amounts of cobalt salts by our silver method and, for comparison, by two of the older methods, Treadwell's and that of Liebig-Gauhe.

A. The Silver Method.—Definite volumes of solutions of $NiSO_4$ and $CoSO_4$ of known concentration were measured from burets into a casserole, KCN was added until the precipitate just dissolved and the solution heated and rotated for five minutes after the change of color was noted. The solution was then diluted with water at 85° to 50 cc., 1 cc. of dimethylglyoxime solution was added, and then silver nitrate dropwise with constant stirring until a permanent precipitate was produced. The time required for the pink color of nickel glyoxime to appear was observed. In cases where the time exceeded one hour, observations were made at the end of twenty-four hours. The results appear in Table II.

TABLE II.

In each expt. 10 cc. $CoSO_4$ 0.0921 *M*, equivalent to 54.31 mg. Co was used.

$NiSO_4$.					
Vol. Cc.	Molar conc.	Ni mg.	Ratio Ni : Co.	Ratio Ni : H_2O. Approx.	Results.
2.0	0.0005	0.0587	1:925	$1:0.85 \times 10^6$	Ppt. pink immediate
1.5	0.0005	0.0440	1:1234	$1:1.14 \times 10^6$	Ppt. pink 4 min.
1.0	0.0005	0.0293	1:1851	$1:1.71 \times 10^6$	Ppt. pink 6 min.
4.5	0.0001	0.0264	1:2054	$1:1.89 \times 10^6$	Ppt. pink 10 min.
4.0	0.0001	0.0235	1:2314	......	Ppt. pink 20 min.
3.5	0.0001	0.0205	1:2644	$1:2.44 \times 10^6$	Ppt. pink 30 min.
3.0	0.0001	0.0176	1:3085	......	Ppt. pink 24 hrs.
2.5	0.0001	0.0137	1:3702	$1:3.65 \times 10^6$	Ppt. pink 24 hrs.

Taking the minimum amount of nickel, 0.0205 mg., which could be detected in cobalt within thirty minutes, we studied the effect of larger proportions of cobalt. The procedure and final total volumes were the same as in the preceding experiments. The results are shown in Table III and indicate that the sensitiveness of the test is not appreciably impaired by the presence of large amounts of cobalt.

TABLE III.

$CoSO_4$. 0.0921 *M*. Cc.	Mg. Co.	Ratio Ni : Co.	Results.
15	81.47	1:3966	Ppt. pink 30 min.
20	108.62	1:5288	Ppt. pink 30 min.
25	135.78	1:6610	Ppt. pink 30 min.
30	162.93	1:7932	Ppt. pink 30 min.

B. The Treadwell Method.—10 cc. portions of 0.0921 *M* $CoSO_4$, equivalent to 54.31 mg. Co, with varying small amounts of $NiSO_4$ were warmed with concentrated ammonia until a clear solution was obtained, hydrogen peroxide was added, and the solutions were heated till excess of peroxide and ammonia was removed, diluted to 50 cc., 1 cc. of dimethylglyoxime solution was added and the time required for the precipitate of nickel glyoximine to appear was observed. The results are given in Table IV.

TABLE IV.

$NiSO_4$.				
Vol. Cc.	Conc. molar.	Mg. Ni.	Ratio Ni : Co.	Results.
10	0.0005	0.293	1:185	Red ppt. 1 hr.
9	0.0005	0.264	1:206	Red ppt. 1 hr.
8	0.0005	0.235	1:231	Red ppt. 1 hr.
7	0.0005	0.205	1:264	Red ppt. 24 hrs.
5	0.0005	0.147	1:370	Red ppt. 24 hrs.
4	0.0005	0.117	1:462	Red ppt. 24 hrs.

Taking the minimum amount of nickel that could be detected in one hour, 0.235 mg., the effect of larger proportions of cobalt was studied. The procedure and final volume of solution were the same as in the experiments recorded in Table IV. The results are shown in Table V. Apparently this method is not very sensitive and fails when much cobalt is present, at least with the small amount of dimethylglyoxime which was used.

TABLE V.

Cc. $CoSO_4$. 0.0921 *M*.	Mg. Co.	Ratio Ni : Co.	Results.
10	54.31	1:231	Red ppt. after 1 hr.
15	81.47	1:346	No ppt. after 1 hr.
20	108.62	1:462	No ppt. after 1 hr.

C. The Liebig-Gauhe Method.—10 cc. portions of $CoSO_4$, 0.0921 *M*, with varying amounts of $NiSO_4$ 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 solution was added. After the precipitate had flocculated, it was filtered off, washed, dissolved in dilute HCl, neutralized with ammonia and tested for Ni with dimethylglyoxime.

TABLE VI.

$NiSO_4$. 0.0005 *M*. Cc.	Mg. Ni.	Ratio Ni : Co.	Results.
9	0.2641	1:206	Blk. ppt. Ni confirmed
6	0.176	1:309	Blk. ppt. Ni confirmed
3	0.088	1:617	Blk. ppt. Ni confirmed
2	0.059	1:925	Blk. ppt. No Ni
1	0.029	1:1850	Blk. ppt. No Ni
None	None	..	Blk. ppt. No Ni

This method appears able to detect 0.1 mg. nickel in a volume of 50 cc., but a confirmatory test must in every case be applied as the precipitate always contains cobaltic hydroxide if the hypobromite is added to a warm solution. Even if the temperature is kept low, $Co(OH)_3$ frequently precipitates.

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 method	0.02 mg.
Treadwell method	0.23 mg.
Liebig-Gauhe method	0.09 mg.

These figures do not adequately convey the relative merits of the three methods, for it should be noted that the Liebig-Gauhe method requires a confirmatory test to make the result quite reliable; 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; moreover, it increases the sensitiveness of dimethylglyoxime about eight times and is 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 (*a*) avoids the use of large amounts of this rather costly reagent; (*b*) 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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NOTE.

An Apparatus for Determining the Ions in a Solution.—In the course of certain work which was being conducted in this laboratory, the following apparatus for the determination of the ions into which a solution dissociates was found to work very satisfactorily. The idea is similar to that expressed by Prof. Stieglitz in his Qualitative Analysis, Vol. I, page 70.

The apparatus is simple and readily constructed, consisting essentially of a U-tube with a means for closing the two arms and for introducing the substance to be tested into the lowest part of the tube. The center part is made by blowing into a piece of glass tubing of about one-half inch diameter a piece of ordinary sized tubing which has previously been drawn out into a fine jet, and fusing to the other end of this latter a thistle tube carrying a small bore stopcock. The large tube is ridged on either side of the jet tube to prevent lateral flowing of the introduced liquid. The side tubes, which are adapters, are connected with the center tube through large bore stopcocks. If the stopcocks are not handy, the side arms may be connected through rubber tubing bearing pinchcocks, although the use of this necessitates the running of two determinations since closing one side may force the liquid over into the other. Platinum electrodes are used.