

and of acids that are soluble in and not oxidized or decomposed by sulfuric acid, are soluble in this solvent.

6. A number of double decomposition reactions between ionized salts in sulfuric acid solution have been described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

## ALPHA-FURILDIOXIME AS A REAGENT FOR THE DETECTION AND DETERMINATION OF NICKEL

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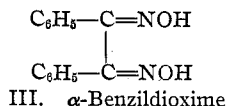
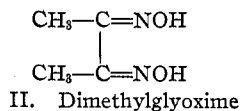
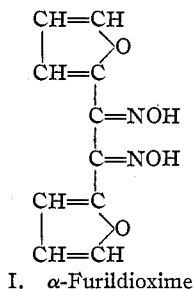
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### Introduction

The change in status of furfural from a laboratory curiosity to a commercial product has made it seem worth while to investigate the properties of its derivative,  $\alpha$ -furildioxime (I), as a reagent for the detection and determination of nickel. Although Tschugaeff<sup>2</sup> mentioned twelve members of the dioxime series, hitherto only two have been studied from the standpoint of their use in chemical analysis. Brunck<sup>3</sup> recommended  $\alpha$ -dimethylglyoxime (II) in 1907, and Atack<sup>4</sup> suggested  $\alpha$ -benzildioxime (III) in 1913. The former reagent is expensive; the latter, while probably the most easily prepared of the  $\alpha$ -dioximes, is so insoluble that it tends to crystallize and contaminate the precipitate. This objection might be overcome by introducing the proper substituent into the benzene ring (perhaps  $-\text{HSO}_3$ ), but to the present time nothing has been found in the literature to indicate that the idea has been tried.

Thus it was with the hope of finding a cheaper, water-soluble  $\alpha$ -dioxime that the properties of  $\alpha$ -furildioxime were investigated.



<sup>1</sup> From a dissertation presented by Byron A. Soule in partial fulfillment of the requirements for the degree of Doctor of Science in the University of Michigan. This work was done under the direction of Professor E. D. Campbell.

<sup>2</sup> Tschugaeff, (a) *Z. anorg. allgem. Chem.*, **46**, 144 (1905); (b) *Ber.*, **41**, 1678 (1908).

<sup>3</sup> Brunck, *Z. angew. Chem.*, **20**, 1844 (1907).

<sup>4</sup> Atack, *Analyst*, **38**, 316 (1913).

## Experimental Part

**Preparation of the Reagent.**—Commercial furfural<sup>5</sup> was used as the starting material for the preparation of  $\alpha$ -furildioxime. The furfural was first converted into furoin and this, in turn, into furil by Emil Fischer's method,<sup>6</sup> slightly modified. Furil melting at about 160° was changed into the  $\alpha$ -dioxime, without purification, by refluxing with hydroxylamine hydrochloride in the presence of methyl alcohol.<sup>7</sup> Though contaminated with a small amount of furoinoxime (?) the product was found to be suitable for the major portion of the quantitative work here described.

Qualitative tests and experiments in which the dioxime was weighed were made with material purified by recrystallization from alcohol. This gave colorless crystals that appeared to effloresce while drying, leaving a white, powdery residue softening and decomposing at 168° (uncorr.).

The dioxime crystals, when used for analytical purposes, were dissolved in sufficient hot water to give a 2% solution, or in sufficient warm alcohol to give a 10% or a 15% solution. As the solutions cooled, some of the solute crystallized; otherwise no change was noted in samples that were made up and left on the work bench for several months in glass-stoppered bottles.

**Standard Nickel Solution.**—Qualitative and preliminary quantitative experiments were performed using a standardized solution prepared from Mond process nickel, containing small amounts of iron and carbon. The metal was converted into nickel sulfate, impurities being removed during the process. The quantity of iron in the product was less than 1 part in 100,000 as indicated by the thiocyanate test. Cobalt could not be detected by Vogel's reaction.<sup>8</sup>

A standard solution was then prepared by dissolving an amount of the nickel sulfate equivalent to 6 g. of metal in 6 liters of water containing 10 cc. of concd. sulfuric acid. Samples of the solution were withdrawn and the amount of nickel in each was determined. The mean of four determinations was 0.001087 g. of nickel per cc. by the electrolytic method and 0.001078 g. per cc. when weighed as nickel dimethylglyoxime. It was found that this value remained constant for several months.<sup>9</sup>

**Delicacy of the Test for Nickel.**—The determination of the delicacy of a test involves two important factors in addition to the amount of substance detectable. The latter is of primary importance, of course, but of almost equal rank are the volume of solution used and the time required for the test. Yet a search of the literature yields few statements of sensitivity accompanied by this information. In the case of dimethylglyoxime we have merely the declaration by Tschugaeff<sup>10</sup> that it will detect less than one part of nickel in 400,000. Atack,<sup>4</sup> when reporting on  $\alpha$ -benzildioxime, was more specific. He stated that "it was found possible to detect immediately less than one part of nickel in 2,000,000 parts of water, using a volume of 5 cc. corresponding to 0.002 mgrm. of nickel."

<sup>5</sup> Furnished by the Miner Laboratories, Chicago, Illinois.

<sup>6</sup> Fischer, *Ann.*, **211**, 218 (1881).

<sup>7</sup> Compare Macnair, *Ann.*, **258**, 226 (1890).

<sup>8</sup> Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, 5th Eng. ed., 1921, Vol. I, p. 192.

<sup>9</sup> Due to similarity of procedure, the second factor was given preference in this investigation.

<sup>10</sup> Tschugaeff, *Ber.*, **38**, 2520 (1905).

It has therefore been deemed advisable to give a somewhat detailed account of the procedure when determining the sensitivity of  $\alpha$ -furildioxime.

Experiments were made to determine the least amount of nickel that could be detected, the test depending upon the formation of a precipitate. This was found to be one part in 6,000,000 parts of solution. The method was as follows.

To 25 cc. of the dilute nickel solution (1:6,000,000) in a test-tube was added about 2 cc. of ammonia water (1:4), then 0.1 cc. of a 10% alcoholic solution of  $\alpha$ -furildioxime. The tube was stoppered and shaken vigorously for 30 seconds, by the watch. Immediate filtration left a distinct red precipitate on the filter paper.

The concentration of ammonium hydroxide was found to be of importance in this test, there being an upper and lower limit for maximum precipitation. Too little aqueous ammonia did not make the solution sufficiently alkaline, too much exercised a solvent effect. The range in one set of experiments was from 1.9 to 2.2 cc.

After determining the sensitivity of the  $\alpha$ -furildioxime reaction, tests were made to see whether  $\alpha$ -benzildioxime would give the same result under the same conditions. All tests were negative. Since  $\alpha$ -dimethylglyoxime is less sensitive, no attempt was made to use it according to the method described.

Assuming the value given by Tschugaeff and Atack to be correct, Table I gives a comparative summary of the sensitivities of the three dioximes.

TABLE I  
SENSITIVITIES OF DIOXIMES TO NICKEL

Reagent	Ratio	Sensitivity Mg. per cc.
Dimethylglyoxime	1:400,000 <sup>11</sup>	0.0025
$\alpha$ -Benzildioxime	1:2,000,000	.0005
$\alpha$ -Furildioxime	1:6,000,000	.00017

A search of the literature has disclosed only one reagent possessing a greater sensitivity to nickel than  $\alpha$ -furildioxime. Potassium dithio-oxalate, according to Jones and Tasker,<sup>12</sup> gives a magneta color easily visible in a test-tube when 1 part of nickel is present in 8,000,000 of solution.

**The Use of  $\alpha$ -Furildioxime in Qualitative Analysis.**—Qualitative tests were, in general, performed by adding a few drops of the reagent to a faintly ammoniacal solution of the substance to be tested. No precipitation or color change was observed in the case of ammonio-silver, -copper, or -zinc. Ammonio-cobaltous solution darkened in color. Results with

<sup>11</sup> Armit and Harden [*Proc. Roy. Soc. (London)*, **77B**, 420 (1906)] give a different value, 1:30,000,000, but do not state the time required for a test.

<sup>12</sup> Jones and Tasker, *J. Chem. Soc.*, **95**, 1908 (1909).

manganese were negative. Ferric iron, chromium or aluminum gave no visible action when tested in ammoniacal solutions containing citrate or tartrate. In fact, with one exception, no ion was found, other than the nickelous, that gave a precipitate under the conditions specified.<sup>13</sup>

The exception was ferrous iron which, in an ammoniacal solution containing less than 1 part in 3,000,000, gave a greenish color. Upon increasing the concentration the color darkened through blue to purple with the final formation of a purple precipitate, either flocculent or in the form of small dendritic crystals, depending upon the speed of separation. This did not obscure the qualitative test for nickel when the concentration of  $\text{Fe}^{++}$  was low, but gave rise to high results in quantitative work where it became an important source of error when the nickel furildioxime was to be weighed.

**Interferences.**—In addition to the difficulty mentioned above, it was found that small amounts of nickel could not be detected in the presence of large amounts of ammonio-cobaltous ion. Oxidation of the cobalt with hydrogen peroxide solved the problem. To avoid precipitation of manganic hydroxide when qualitatively testing for nickel in a solution containing manganese, it was found that Brunck's expedient<sup>14</sup> worked satisfactorily, namely, performing the test in the presence of acetic acid and sodium acetate. This modification also gave good results in the presence of cobalt and zinc.

It should be emphasized that purified  $\alpha$ -furildioxime was used for the qualitative work. An impure sample gave tests with several of the ions mentioned, particularly copper and cobalt. The precipitates appeared the same as those obtained when using furoinoxime in another investigation.<sup>15</sup> It is possible that this compound was the interfering impurity.

#### The Use of $\alpha$ -Furildioxime in Quantitative Analysis

**Composition of the Precipitate.**—The composition of nickel furildioxime was determined, as regards the nickel content, by Chosinsky working under the direction of Tschugaeff.<sup>16</sup> Details of the method were not given other than that the nickel was weighed as nickelous oxide. Chosinsky obtained results corresponding to 11.85% of nickel for the formula  $\text{C}_{22}\text{H}_{14}\text{N}_4\text{O}_6\text{Ni}$ , whereas the calculated value is 11.81%. No specific attempt was made to check this figure, since calculations involving data obtained in various experiments indicated that it was correct.

The nickel contents of the related compounds, derived from dimethylglyoxime and benzildioxime, are given in Table II.

<sup>13</sup> Platinum and palladium give precipitates but have not been considered in this investigation.

<sup>14</sup> Brunck, *Z. angew. Chem.*, **20**, 1844 (1907).

<sup>15</sup> Compare Feigl, *Ber.*, **56**, 2083 (1923).

<sup>16</sup> Ref. 2 b, p. 1681.

TABLE II  
NICKEL CONTENT OF THE DIOXIMES

Nickel Ni content, %	Dimethylglyoxime	Benzildioxime	Furildioxime
	20.32	10.93	11.81

It will be seen from Table II that the quantity of nickel in the two-ring compounds is about half that in the dimethyl derivative, and that there is a difference of less than 1% between the value for  $\alpha$ -benzil- and that for  $\alpha$ -furildioxime, which is negligible as a basis for choice in analytical work.

**Preliminary Analyses.**—Preliminary experiments were made to determine the effect of the various reagents used in the determination of nickel. First, separation in the presence of ammonium salts was tried. This was followed by a study of the effect of the common compounds used to prevent the precipitation of iron. Some of the results obtained are given in Table III. It will be seen from these data that the compounds considered do not interfere.

Precipitation is quantitative from solutions containing up to about 65% of alcohol. With higher concentrations the solubility increases and the precipitate formed is crystalline.<sup>17</sup>

**Method of Analysis.**—Known volumes of the standard nickel solution, corresponding to about 0.02 g. of nickel, were taken for analysis. Larger samples were found to be difficult to handle owing to the bulky nature of the precipitate. Each sample was diluted with 100 cc. of water. The desired salt or acid was then added, followed by ammonia water (28%) until a faint odor of ammonia was perceptible. In some cases an excess of dioxime solution was next slowly added during stirring; in others, preliminary heating to various temperatures was tried. An amorphous, red precipitate was obtained upon introduction of the reagent. When the precipitate showed a tendency to float, vigorous stirring for a few minutes accompanied by cooling caused it to sink to the bottom of the beaker. After a short time the mixture was filtered and washed with warm water. The paper, with contents, was transferred to a beaker and treated with 1:1 nitric acid. Warming caused the dioxime to dissolve and the paper to disintegrate. The paper pulp was removed by filtration and the filtrate evaporated after addition of concd. sulfuric acid. Elimination of the excess of nitric acid and organic matter was thus effected. The residue was diluted, made ammoniacal and electrolyzed.

During the preliminary investigation care was taken to remove the last traces of organic matter and to secure an electrolyte having the characteristic color of an ammoniacal nickel solution. It was discovered, however, that this was unnecessary. Solutions varying from dark red through yellow to violet, were electrolyzed with no apparent difficulty or difference in results.

<sup>17</sup> Brunck [*Z. angew. Chem.*, **27**, (I) 315 (1914)] states that alcohol exercises a solvent effect on nickel dimethylglyoxime when present in large quantity.

TABLE III  
QUANTITATIVE SEPARATION OF NICKEL FROM SOLUTIONS CONTAINING VARIOUS COM-  
POUNDS USED IN ANALYSIS

Substance added	Ammonium salts			
	Amount G.	Ni taken G.	Ni recov. G.	Diff. Mg.
Chloride.....	2	0.0218	0.0218	0
Chloride.....	3	.0218	.0218	0
Sulfate.....	2	.0225	.0226	+0.1
Sulfate.....	4	.0217	.0216	- .1
Nitrate.....	2	.0217	.0215	- .2
Compounds used to prevent precipitation of ferric iron				
Citric acid.....	2	0.0277	0.0279	+0.2
Sodium citrate.....	2	.0217	.0218	+ .1
Tartaric acid.....	2	.0217	.0216	- .1
Sodium tartrate.....	2	.0217	.0217	0
Sodium pyrophosphate.....	2	.0218	.0217	-0.1

**Determination of Nickel in the Presence of Iron.**—The method described above was used for the analysis of samples containing various amounts of iron, added in the form of a standard solution of ferric sulfate, prepared from very pure electrolytic iron. Results are given in Table IV.

TABLE IV  
DETERMINATION OF NICKEL IN THE PRESENCE OF IRON

Ni taken G.	Fe taken G.	Added to prevent pptn. of Fe <sup>a</sup>	Ni recov. G.	Diff. Mg.
0.0054	0.50	Sodium citrate	0.0054	0
.0216	.50	Sodium citrate	.0219	+0.3
.0216	.50	Citric acid	.0218	+ .2
.0216	.10	Citric acid	.0216	0
.0216	.20	Citric acid	.0215	-0.1
.0108	.50	Sodium tartrate	.0108	0
.0217	.30	Sodium tartrate	.0217	0
.0217	.10	Tartaric acid	.0217	0
.0216	.30	Tartaric acid	.0217	+0.1

<sup>a</sup> 4 g. was added in each case.

**Determination of Nickel in the Presence of Manganese, Zinc and Cobalt.**—The use of  $\alpha$ -furfildioxime for the separation of nickel from manganese, zinc or cobalt offered no especial advantages over dimethylglyoxime. The method involving precipitation in an acetic acid-sodium acetate solution, as recommended by Brunck,<sup>3</sup> was not found particularly satisfactory for the quantitative removal of nickel from a manganous solution.<sup>18</sup> Zinc was most easily separated in an ammoniacal solution containing ammonium salts. Cobalt solutions were not difficult to handle when the cobalt was in the trivalent, ammoniacal form.

<sup>18</sup> A further study of this problem is being made.

**Determination of Nickel in Steel.**—Analyses were made of three different samples of Bureau of Standards steels. The preparation for precipitation was practically the same for all tests. A typical case follows.

To a solution of 0.7 g. of steel in 50 cc. of 1:2 nitric acid was added 5 cc. of hydrochloric acid. The solution was diluted with 200 cc. of water and heated almost to the boiling point. Then 6 g. of citric acid in about 15 cc. of water was added, followed by 34 cc. of ammonia water, bringing the total volume up to 300 cc. and also giving the proper alkalinity.

Following the precipitation of nickel furildioxime, various methods were tried for determining the quantity of metal present.

**Gravimetric.**—Data for Sample 2, Table V, were obtained by collecting the dioxime precipitate on a filter paper, drying at 120–130° and weighing.<sup>19</sup>

As a check, the precipitate was ignited to nickelous oxide in a covered crucible. Burning took place quietly between 250° and 300°, without sublimation.<sup>20</sup> After the oxide had been weighed it was converted to the sulfate and electrolyzed.

The precipitates of Samples 2 and 3 were collected in Gooch crucibles, dried and weighed.

Determinations 4 to 7 were made by the electrolytic method already described.

TABLE V  
THE DETERMINATION OF NICKEL IN STEEL BY GRAVIMETRIC METHODS AFTER SEPARATION AS NICKEL FURILDIOXIME

No.	Sample G.	Wt. dioxime G.	STEEL 33a: Ni, 3.24% <sup>a</sup>				
			Equiv. to Ni %	Ignited to NiO G.	Equiv. to Ni %	Electrolysis Ni G.	Equiv. to Ni %
1	0.7004	0.1943	3.28	0.0293	3.27	0.0227	3.24
2	.7004	.1943	3.28	...	..	...	..
3	.7025	.1946	3.27	...	..	...	..
4	.7559	...	..	...	..	.0247	3.26
STEEL 32a: Ni, 1.58%; Cr, 0.89% <sup>a</sup>							
5	1.0033	...	..	...	..	.0157	1.56
6	1.0560	...	..	...	..	.0167	1.58
7	1.0313	...	..	...	..	.0162	1.57

<sup>a</sup> Bureau of Standards Certificate.

There is one point to be noted in connection with the procedure mentioned for the first three samples. As stated in the section dealing with qualitative tests, ferrous iron gives a purple precipitate with  $\alpha$ -furildioxime. It has long been known that citrates and tartrates reduce ferric to ferrous iron, especially in the sunlight.<sup>21</sup> Hence when either ion is used to prevent

<sup>19</sup> Iwanicki, *Stahl u. Eisen*, **28**, 1546 (1908).

<sup>20</sup> Brunck (Ref. 3) noted that nickel dimethylglyoxime sublimes when heated above 250°.

<sup>21</sup> Schoras, *Ber.*, **3**, 111 (1870).

the precipitation of iron, there is danger of contaminating the nickel furildioxime with ferrous furildioxime. The difficulty can be minimized by filtering within one-half hour after precipitation, or it can be avoided by the use of sodium pyrophosphate.

**Cyanide Titration.**—Precipitates were separated by use of filter paper and transferred to beakers. Addition of 15 cc. of nitric acid, followed by heating, quickly dissolved the precipitates and destroyed the major portion of the organic matter. The solutions were diluted and filtered. A few crystals of ammonium persulfate were added to the filtrates which were then heated to insure destruction of traces of organic matter. Subsequent steps were according to the procedure described by Campbell and Andrews<sup>22</sup> for the determination of nickel by cyanide titration. The results for four consecutive samples are given in Table VI.

TABLE VI  
NICKEL DETERMINED BY SEPARATION AS NICKEL FURILDIOXIME FOLLOWED BY CYANIDE TITRATION

	Bureau of Standards Steel No. 33 containing Ni 3.33%			
Sample, g.....	0.7201	0.7096	0.7720	0.8289
KCN <sup>a</sup> , cc.....	25.20	24.70	27.00	28.80
Ni found, %.....	3.33	3.32	3.34	3.32

<sup>a</sup> 1 cc. of KCN  $\approx$  0.00095 g. of Ni.

### Summary

1.  $\alpha$ -Furildioxime may be used to detect one part of nickel in 6,000,000 of solution.
2. Ferrous iron is the only other common metal ion that gives a precipitate with the reagent. Ammonio-cobaltous ion must be oxidized to prevent interference with the precipitation of nickel.
3. The reagent is sufficiently soluble in hot water to make possible the use of an aqueous solution.
4. In quantitative work the precipitate of nickel furildioxime may be weighed directly, ignited to nickelous oxide, or dissolved and the nickel determined by electrolysis or cyanide titration.

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<sup>22</sup> Campbell and Andrews, *Am. Chem. J.*, **17**, 164 (1895).