

Studies in
Micro-Estimation of Metallic Elements.
Part II. The Micro-Detection of Iron with
Dimethylglyoxime.

By

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The possibility of use of dimethylglyoxime for detection of a minute quantity of cobalt was pointed out by Prof. M. Matsui in 1918. He has also called attention to the production of a red color by the action of dimethylglyoxime upon a solution of ferrous salt when the mixture was treated with hydrogen sulfide and neutralized with ammonia. At his suggestion the following experiments were performed to ascertain the conditions of this reaction in more detail.*

I. The standard ferrous ammonium sulfate solution containing 0.1 mg. of Fe in 1 cc. was used as the stock solution for preparing various dilutions of the test solutions of iron. Dimethylglyoxime used was dissolved in alcohol to one per cent. strength. The hydrogen sulfide solution was always used in the freshly saturated state. The solutions were mixed in the order, from left to right, given in the table below, and the nature of the color developed was carefully noted 10 minutes after mixing the reagents.

With solutions containing 0.05–0.1 mg. of Fe in the final volume of 2.5 cc. there appeared, immediately on addition of saturated hydrogen sulfide solution, a more or less distinct opalescence due to the liberation of some free sulfur, which, however, caused no harm to the observation of the result.

* M. Matsui: J. Tokyo Chem. Soc., **39**, 463 (1918).

The solutions containing 0.4 and 0.2 mg. of Fe showed, when diluted to 50 cc., a presence of abundant minute black particles floating about but having no tendency to settle down. The color of the solution itself was dark wine red. On being allowed to stand several hours, the black particles have partly dissolved away and partly settled on the bottom.

The solution containing 0.1 mg. of Fe showed, when diluted to 50 cc. no black particles in it and the liquid was dark wine red. The solution containing 0.05 mg. of Fe was, when diluted to 50 cc., pure beautiful orange and became opalescent suddenly after 30 minutes.

The solutions containing in the final volume of 2.2 cc. 0.01 and 0.005 mg. of Fe were beautiful wine red. When diluted to 10 cc., the color changed to a very thin but pure orange. The solutions with 0.001 and 0.0005 mg. of Fe respectively in the final volume of 2.2 cc. were very faint orange which became only just barely perceptible by diluting to 10 cc.

No.	Fe taken mg.	H ₂ S cc.	Dimethyl- glyoxime	6-N ammonia	Final volume	Color of the mixture after 10 minutes.
			drops	drops	cc.	
1	0.4	1	10	5	5.5	Intensely dark red, almost black.
2	0.2	1	10	4	3.5	Intensely dark red, almost black.
3	0.1	1	10	4	2.5	Intensely dark red.
4	0.05	1	10	3	2.3	Intensely dark red.
5	0.01	1	10	2	2.2	Brownish red.
6	0.005	1	10	2	2.2	Brownish red.
7	0.001	1	10	2	2.2	Slight pink orange.
8	0.0005	1	10	2	2.2	Very faint pink orange.
9	0.0001	1	10	2	2.2	Extremely faint orange.
10	0.00005	1	10	2	2.2	Almost imperceptibly faint orange.

The solutions containing in the final volume of 2.2 cc. 0.0001 and 0.00005 mg. of Fe respectively were extremely faint orange and well-nigh imperceptible unless a very close comparison was made with pure water. Thus, 5/100 000 mg. of Fe in 1 cc. of the original and in 2 cc. of the final volume is the minimum quantity detectable by means of the dimethylglyoxime reaction.

Quantities of Fe ranging between 0.1 and 0.01 mg. are best estimated

in the volume of 50 cc. by the colorimetric comparison of the dimethylglyoxime reaction. For quantities ranging between 0.001 and 0.01 mg. of Fe, a volume of 10 cc. is more suitable for the colorimetric purpose.

II. In the second series of experiments, the order of mixing the reagents was changed in such a manner as to make the saturated H_2S solution come at last. It was found that a mixture of iron solution and dimethylglyoxime reagent developed a beautiful reddish yellow on making it alkaline with ammonia. When H_2S was added to this solution, the color changed to dark green, separating at the same time minute black particles floating about without any tendency to settle down. When the quantity of H_2S added was small, the solution became opalescent in a few minutes; with a larger quantity of H_2S , opalescence did not appear within two hours.

No.	Fe taken	Dimethylglyoxime	6-N Ammonia	H_2S	Color developed	Opalescence appeared
	mg.	drops	drops	drops		
1	0.1	10	2	5	Reddish yellow by ammonia, changing to dark green by H_2S .	5 min.
2	0.1	10	2	10	The same as above	15 min.
3	0.1	10	2	15	The same as above	2 hrs.
4	0.1	10	2	20	The same as above	12 hrs.

III. For the purpose of ascertaining any difference, if there be, between ferrous and ferric salts in their dimethylglyoxime reaction, the following experiments were repeated several times always with the concordant results.

1. One cc. of ferrous ammonium sulfate solution containing 0.1 mg. of Fe was boiled with 1 cc. 1-N NaHSO_3 solution with addition of 1 drop of 6-N HCl . No change of color was observed by adding to this 10 small drops of dimethylglyoxime solution. There were now added 2-3 drops of ammonia, when a beautiful red color appeared, which changed, on addition of an excess of saturated H_2S , into a very dark brownish red. On dilution to 50-60 cc. the color changed to brownish orange.

2. One cc. of the solution containing 0.1 mg. of Fe was boiled with 2 drops of bromine water with addition of 1 drop of 6-N HCl . No change of color was noticed by adding to this 10 drops of dimethylglyoxime solution. By adding now 2-3 drops of 6-N ammonia,

there appeared a beautiful yellow color which changed, on addition of an excess of saturated H_2S , into a very dark green. By diluting to 50-60 cc., the color remained dark green almost without any tint of yellow or red. There were also noticed abundant black particles floating in the dark green solution. These particles were very light and did not show any tendency to settle down in the course of several hours. By allowing to stand over night, these particles were found to have partly dissolved away and partly settled on the bottom.

IV. A comparison of dimethylglyoxime and ammonium sulfocyanate as the reagents for micro-detection of iron was instituted. For testing with the former reagent the standard ferrous ammonium sulfate solution was diluted to such a strength as 1 cc. of it contained 0.001 mg. of Fe. For testing with the latter reagent, 2 cc. (0.002 mg. Fe) of the ferrous ammonium sulfate solution were boiled with 2 drops of bromine water and 2 drops of 6-N HCl, evaporated to near dryness, and made up to 2 cc. Four different quantities of each solution were taken for the testing purpose.

No.	Ferrous iron		H_2S	Dimethylglyoxime	6-N ammonia	Color	Color-maximum reached in
	solution	Fe					
	drops	mg.					
1	20	0.001	1	1	2	Faint orange	2 hrs.
2	10	0.0005	1	1	2	Very faint orange	2 hrs.
3	2	0.0001	1	1	2	Extremely faint orange	2 hrs.
4	1	0.00005	1	1	2	Still perceptible orange	2 hrs.

No.	Ferric iron		Ammonium sulfocyanate	Color	Color-maximum reached in
	solution	Fe			
	drops	mg.			
1	20	0.001	1	Faint red	a few minutes.
2	10	0.0005	1	Very faint red	a few minutes.
3	2	0.0001	1	Extremely faint red	a few minutes.
4	1	0.00005	1	No color	

The detectability of iron, or the degree of color distinctness, with the both reagents was about the same when the quantities ranged between 0.001 and 0.0001 mg. of Fe. With 0.00005 mg. of Fe, the faint pink orange of dimethylglyoxime was barely but undubitably perceptible, while there was no color noticeable with NH_4SCN reagent.

SUMMARY

1. The color tone and the color depth produced by the action of dimethylglyoxime upon iron solutions change with the change of the order of mixing the reagents. But they remain constant so long as the concentration of the reagents and the order of mixing them remain the same.

2. If the dimethylglyoxime test of iron is made with a sufficient excess of H_2S , the color developed is very intense and it keeps well for twenty hours or more. The color depth is also proportional to the concentration of iron.

3. The presence of an excess of H_2S is also necessary to prevent the opalescence of the reaction mixture. The iron-dimethylglyoxime-hydrogen sulfide compound is rather unstable and, in small concentrations of H_2S , it fades in color and liberates sulfur as opalescence. When it has once undergone this change, the original color can no more be restored by again saturating the solution with H_2S .

4. For the purpose of colorimetric estimation of minute quantities of iron with dimethylglyoxime, the test solution should be first treated with saturated H_2S solution so as to reduce any ferric salt present to ferrous salt. The mixture should then be treated with dimethylglyoxime and finally with ammonia.

5. The applicability and utility of dimethylglyoxime and ammonium sulfocyanate for micro-colorimetry of iron are about the same in the both cases, although one may be used in preference to the other according to circumstances.

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