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THIOGLYCOLIC ACID AS A COLOR TEST FOR IRON

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The standard method for the identification of ferric iron is the thiocyanate method. The test is based on the red color formed when an alkali thiocyanate reacts with ferric iron in acid solution. This method, with various modifications, is used for the determination of small amounts of iron.

For the detection of ferrous iron in minute quantities, the dark blue ferrous ferricyanide test is used. This serves to indicate the presence of ferrous iron in ferric solutions.

The test under consideration in this paper is the color produced when the reaction mixture between thioglycolic acid and iron in solution is made faintly alkaline. The color so produced has long been known. Andreasch[1] described it in detail and Claësson[2] claimed that he was quite aware of the reaction. The interpretation of the reaction, however, we believe to be entirely different from what they claim. They believed that the color produced was due to the formation of the complex ferric thioglycolate, $Fe(SCH_2COONH_4)_3$. They further observed that the color faded after some time but was regenerated on shaking the solution with air. The fading of the color, they thought, was due to oxidation of part of the acid which then gave a colorless ferro salt. This in turn took up oxygen and gave the colored ferri salt. We differ entirely with the explanation of the mechanism of the color reaction as given by the above-mentioned investigators. The test has been found to be general for both ferric and ferrous iron. The red or purple color produced, however, is due to the reaction between ferrous iron and thioglycolic acid. In alkaline solution the color produced is pink in dilute solutions and intensely reddish-purple in the more concentrated solutions. The test is applicable quantitatively in dilutions approximating one part of iron in about five million. Qualitatively, iron can be detected even in dilutions of 1:10 or 12 million. With thiocyanate the quantitative estimation of ferric iron in dilutions greater than several parts of iron per million presents considerable difficulty in color matching.

When ferric iron in concentration greater than 1:100,000 is present, the addition of thioglycolic acid yields a transient blue coloration. When the concentration is less, only a flash of blue may be observed. This is due to the formation of ferric thioglycolate, $Fe(SCH_2COOH)_3$. However, this is at once reduced to the colorless ferrous thioglycolate, Fe-

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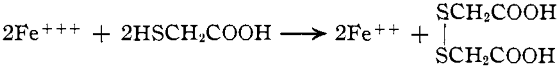
[1] Andreasch, *Ber.*, **12**, 1391 (1879).

[2] Claësson, *Ber.*, **14**, 411 (1881).

$(SCH_2COOH)_2$, complex, which yields the intensely colored ferrothioglycolate ion, $Fe(SCH_2COO)_2^{--}$, in alkaline solution. If thioglycolic acid is similarly added to a solution of ferrous iron the blue coloration does not appear at all, but an intense red color is formed on making it alkaline. The presence of an oxidizing substance prevents the formation of the color. This is probably due to the formation of dithioglycolic acid, which does not yield color with either ferrous or ferric iron; its formation is the cause of the color fading observed by the previous investigators. The color cannot be regenerated by "shaking with air" nor by passing oxygen gas through the solution. On the contrary, fading of color results and when all of the thioglycolic acid has been oxidized the color can be brought back only by addition of more thio acid, or by means of a reducing agent which regenerates the thio acid in solution. Using ferric iron in the test and discharging the color formed with concd. hydrochloric acid, we no longer obtain a test for iron with thiocyanate, thus showing that the iron has been reduced to the ferrous condition. The addition of a drop of peroxide also discharges the color. It oxidizes not only the thio acid, but in the resulting solution thiocyanate gives a test for ferric iron.

The mechanism of the reaction between ionic iron and thioglycolic acid is probably best expressed as follows.



$$2Fe^{+++} + 2HSCH_2COOH \longrightarrow 2Fe^{++} + \begin{array}{l}SCH_2COOH\\ | \\ SCH_2COOH\end{array} \qquad (1)$$

$$Fe^{++} + 2(SCH_2COOH)^{-} \longrightarrow \underset{\text{Colorless}}{Fe(SCH_2COOH)_2} \longrightarrow \underset{\text{Colored}}{Fe(SCH_2COO)_2^{--}} \qquad (2)$$

Reaction 1 occurs only when Fe^{+++} is present. As soon as it is reduced, Reaction 2 takes place, yielding the colored ion when an alkali is added. However, if an excess of acid or alkali is added the color is discharged. Neutralization of the excess reagent added again brings out the color.

Although the reaction is between ferrous iron and thioglycolic acid, both ferric and ferrous iron may be detected and estimated in the same solution. The color with thiocyanate due to ferric iron, which is stable in acid solution, is readily discharged by alkalies, while that produced by thioglycolic acid is stable in weakly alkaline solutions. Strong bases have to be used with considerable care, since a small excess discharges the color. Ammonia, however, does not appear to affect the intensity of the shade quickly, even when present in great excess. In time, however, a too great amount will show its effect. Since thioglycolic acid reduces ferric to the ferrous form, the total iron present can be readily estimated. The ferric iron can be determined with thiocyanate and the ferrous iron is then obtained by difference.

Qualitative Test.—To about 5 cc. of the suspected neutral or slightly acid solution free from oxidizing agents (these oxidize the thio acid), add one drop of thioglycolic acid and about 0.5 cc. of concd. aqueous ammonia.

If no color appears in about five minutes, no ionic iron is present in concentration greater than 1 to 10 or 12 million. When iron is present in concentration of 1 to 4 or 5 million or greater, the color appears at once. If it is of interest to know whether any ferric iron is present, a test with thiocyanate can be made first; then a drop of thioglycolic acid is added, and on addition of aqueous ammonia, in excess, the color due to ferric iron (if present) fades and the purple or pink color due to the ferrous-thioglycolic acid reaction appears. When the ammonia is added before the thio acid the maximum intensity of color appears somewhat more slowly.

The intensity of the color obtained with different concentrations of iron solutions led us to believe that the method would be applicable quantitatively. Accordingly, a series of solutions was made containing one part of iron in 100,000, 200,000, 300,000, etc., up to 12 millions. These were then used as unknowns. It was found that the difference between every two dilutions could be very easily detected and the particular concentration dealt with absolutely determined by comparison with known standards of similar solutions up to about 1 in 4 or 5 million parts. In greater dilutions the results were only qualitative. From these results we were able to develop a method for the determination of ferrous and ferric iron in any solution.

Quantitative Estimation of Total Iron (Ferric plus Ferrous)

(a) **Total Iron.**—The unknown solution is first tested qualitatively. From the intensity of the color obtained, a little experience soon teaches the experimenter to approximate the correct concentration. The dilution is then adjusted to about 1:500,000. When the solution is already very dilute the determination is made on the original, if feasible, or the solution is concentrated by evaporation. In the present work the color produced at about 1:500,000 was used. At this dilution the colors obtained are very easy to match, and the difference in intensity between, say 475,000 and 500,000, is distinct enough to allow an approximation of the intermediate dilutions very nicely. The solution prepared for testing is then transferred to a test-tube marked at 5cc. volume. To this is now added one drop of thioglycolic acid and 0.5 cc. of concd. aqueous ammonia. The color produced is then compared with the colors of standards of known concentration of iron. We then have: % Fe in unknown $= 100 \times \frac{\text{dilution of unknown}}{\text{dilution of standard}} \div$ amount used (g. or cc.); multiplying by 10,000 we have parts per million; that is, if 1.0 cc. of an unknown is diluted to a final volume of, say, 5000 and compared with a 1:400,000 standard, then % Fe in unknown $= 100 \times (5000/400,000) \div 1 = 1.25$, or 12,500 parts per million.

Likewise, if 0.2 g. of substance is dissolved to give a solution containing one part in 10,000, and the color of this agrees with that of a 1:300,000 standard, then % Fe = 100 × (10,000/300,000) ÷ 0.2 = 0.067.

(b) **Ferric Iron.**—By using potassium thiocyanate in a hydrochloric acid solution of the unknown and comparing with colors of standard solutions, the ferric iron may be estimated as usual. If the sample at hand is not of sufficient quantity to permit a separate determination, then both ferric and ferrous iron may be determined in the one sample before the estimation of the "total iron." A drop or two is tested with potassium thiocyanate. If ferric iron is indicated, a quantitative estimation on the major part of the sample is made. This gives us the ferric iron. To this solution is now added a few drops of aqueous ammonia, to discharge the color due to ferric iron, the ammonium hydroxide is neutralized with hydrochloric acid, since it delays the appearance of the color, then one drop of thioglycolic acid is added. Ammonium hydroxide now added in slight excess gives the color due to the total iron reduced to the ferrous condition.

(c) **Ferrous Iron.**—From the total iron (estimated as ferrous) subtract the ferric iron (potassium thiocyanate method). The difference is the ferrous iron originally present.

TABLE I

DETERMINATION OF IRON IN SOME SAMPLES

Substance	Iron found	Iron by analytical method, or calcd.	Remarks
Sol. Fe Chloride	10.0%	10.2%	
Colloidal Fe Soln.	0.0114 g. per cc.	0.0119 g. per cc.	Decomp. with HCl
$FeSO_4(NH_4)_2SO_4.6H_2O$	14.02%	14.25%	
U. S. P. Iron Quinine Citrate	12.5%	13.00±%	
Iron Cacodylate	0.00155 g. per cc.	0.00160 g. per cc.	

TABLE II

ANALYSIS OF MIXTURES OF FERROUS AND FERRIC IRON

Mixtures containing known amounts of ferric and ferrous iron were made. Ferric iron was determined by the potassium thiocyanate method. Total iron was obtained by the thioglycolic acid method. The difference gave the ferrous iron.

Ferric iron, g.		Total iron, g.		Ferrous iron, g.	
Taken	Found	Taken	Found	Taken	Found by diff.
0.0001	0.0001	0.00015	0.00016	0.00005	0.00006
.00018	.0002	.00026	.0003	.00008	.00010
.00004	.000036	.00018	.00018	.00014	.000144

The following substances (0.01 g. per cc. of 1:500,000 ferric solution) did not appear to affect the delicacy of the reaction.

Sodium acetate, arsenate, bromide, benzoate, citrate, cacodylate, chloride, fluoride, glycerophosphate, iodide, phosphate, pyrophosphate, salicylate (use three or four drops of thio acid), sulfate, sulfite, sulfocarbolate, thiosulfate, etc.

Also salts of the following metals: potassium, lithium, barium, calcium, strontium, and, if not in too large amounts, mercury, copper, cadmium, zinc, tin, magnesium, silver, bismuth, etc. When these are present in the order of the concentration of the iron no interference is observed (especially when three or four drops of thio acid are used). Large amounts (0.001 g. per cc. or more) which of themselves give a color with the acid or tend to precipitate with aqueous ammonia may affect the delicacy of the test. The addition of some sodium citrate will in such cases often bring out the full color due to the iron present.

Summary

Thioglycolic acid is recommended as a delicate color test for iron. This reagent[3] is capable of detecting iron in dilutions up to 1:10,000,000 and is relatively much more delicate than the usual thiocyanate test. Moreover, the test is independent of the state of oxidation of the iron since it is given equally well with either ferrous or ferric iron in contrast with the thiocyanate test which is sensitive only to ferric iron.

A study of the reaction of thioglycolic acid with iron has shown that the reagent is really a test for ferrous iron, but since the reagent itself promptly reduces ferric iron to the ferrous state we have here a general test for ionic iron.

Since the thioglycolic acid test is applied in ammoniacal solution, a condition under which the color obtained with ferric iron and thiocyanate is completely discharged, the two tests may be applied to the same solution in succession.

The thioglycolic acid test is capable of quantitative application. Used in conjunction with the thiocyanate test we have here a simple method of estimating both ferric and ferrous iron in the same solution by colorimetric methods.

DETROIT, MICHIGAN

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[3] Thioglycolic acid is now being supplied by the Eastman Kodak Co.