THE DETECTION OF COPPER WITH PHENOLPHTHALIN-CYANIDE REAGENT.

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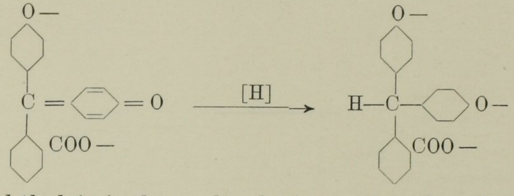
Phenolphthalein is easily reduced to phenolphthalin by boiling with zinc in alkaline medium:



Phenolphthalein is thus o-di-p-hydroxy phenyl methyl benzoic acid which is colorless in alkaline medium and readily oxidized again to phenolphthalein. According to J. STAMM[1] this oxidation even occurs when the alkaline solution stands in contact with air. F. WEEHUIZEN[2] made use of the phenolphthalin reagent for the detection of cyanide in the presence of copper as a catalyst, and it has been investigated further by I. M. KOLTHOFF[3] and by J. STAMM[1].

The mechanism of this oxidation is not entirely clear. Various authors[4] claim that cupric cyanide is formed which decomposes with the formation of cuprous cyanide and O or O_3. To the present authors

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[1] Pharmacia **16**, 1 (1924).

[2] Pharmac. Weekbl. **42**, 272 (1905).

[3] Ztschr. analyt. Chem. **57**, 11 (1918).

[4] For literature compare STAMM, ref. 1.

it seems that the effect of copper is catalytic. The cyanagen formed in the decomposition of the cupric cyanide probably oxidizes the phenolphthalinate to phenolphthaleinate, and part of the cuprous cyanide is reoxidized to the cupric state by oxygen from the air; the reaction can thus go on indefinitely. This view is supported by the fact that the reaction was found to be greatly inhibited when air was displaced from the solution by hydrogen. In a typical experiment the reaction was carried out according to the procedure given below with a solution containing 1 mg. of copper per liter, 10 ml. of which were placed in each of two test tubes provided with sealed in outlet and inlet tubes for gases [5]. Purified hydrogen was bubbled through one solution for thirty minutes to remove air and the other solution was left in contact with air, the reagents were then added quickly to both samples. The solution that had been freed from air gave only a slight reaction, very much less than the solution containing air, the slight reaction in the air-free solution was probably due to the introduction of a small amount of air with the reagent solutions, but the experiment proves conclusively that oxygen from the air is involved in the reaction. The striking difference between the two tests suggests a study of the application of the reaction to the detection of traces of oxygen.

J. H. KASTLE and O. M. SHEDD [6] used phenolphthalin reagent for the detection of vegetable oxydases, and MEYER [7] for the detection of blood. P. THOMAS and G. CARPENTIER [8] used phenolphthalin and hydrogen peroxide in alkaline medium as a reagent for the detection of copper. To 10 ml. of solution, they add 4 drops of the alkaline phenolphthalin reagent and 1 drop of hydrogen peroxide (5—6 vol%). In the presence of 1 mg of copper per liter the solution becomes pink immediately, 0,1 mg. per liter after 15—20 seconds, and 0.01 mg. per liter after several minutes (limit of sensitivity). A blank without copper did not give a reaction, even after standing for 5 hours. The reaction of THOMAS and

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[5] I. M. KOLTHOFF and TOHRU KAMEDA, Journ. Am. chem. Soc. **53**, 829 (1931).

[6] Amer. chem. Journ. **26**, 527 (1901).

[7] Münchner Mediz. Wochenschr. **50**, 1492 (1903).

[8] Compt. rend. **173**, 1082 (1921).

Carpentier is recommended by J. C. Thresh[9] for the detection of copper in potable water. Although, regarding the sensitivity of the test our results agreed with those of Thomas and Carpentier[7], it was found that the reaction should not be applied to the detection of copper in natural waters because magnesium interferes. Apparently, the magnesium hydroxide formed on addition of the alkaline reagent adsorbs all the copper from solution, and the latter remains colorless even in the presence of appreciable amounts of copper. In order to prevent the interference by magnesium we tried to reduce the alkalinity by working with a buffer of ammonia and ammonium chloride. However, under these conditions the hydrogen peroxide alone gives a pink color with the reagent, although it does not oxidize the phenolphthalin in strongly alkaline medium.

Since it was found in previous work[3] that the test for cyanide with copper as a catalyst gave the most sensitive results in weakly alkaline medium, the detection of copper with phenolphthalin and cyanide in a buffer of ammonia and ammonium chloride was studied in detail. The procedure given below allows the detection of traces of copper even in the presence of large amounts of magnesium and is recommended for the detection of copper in natural waters.

Reagents; Phenolphthalin reagent; Heat a solution of 0.5 g. of phenolphthalein in 100 ml. of 1 N sodium hydroxide with an excess of 20 mesh granulated zinc for one hour on a boiling water bath. Complete reduction is indicated by the disappearance of the red color. After cooling, the excess zinc is left in contact with the solution to prevent air-oxidation of the phenolphthalin.

6 N Ammonium hydroxide.

4 N Ammonium chloride.

1 per cent potassium cyanide solution.

Procedure: Add to 10 ml. of the approximately neutral solution 5 drops of ammonia, 5 drops of ammonium chloride, 5 to

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[9] Examination of Water and Water Supplies, 3rd edition, P. Blakiston Son & Company. 1925, p. 311.

10 drops of potassium cyanide, and 4 drops of the phenolphthalin reagent. The appearance of a pink to red color denotes the presence of copper.

Sensitivity:

1 mg. of Cu per liter: Color occurred after a few seconds.
0.1 mg. of Cu per liter: Color occurred after 15 seconds.
0.01 mg. of Cu per liter: Color occurred after 3 minutes.
0.005 mg. of Cu per liter: Slight color after 15 minutes.
0.0025 mg. of Cu per liter: Very slight color after 30 minutes but no difference from blank.

Blank in redistilled water: Very slight color after 30 minutes.

According to the data given above, the reaction is sensitive to 0.005 mg. of copper per liter (or 0.05 γ in 10 ml.) when the color is observed 15 minutes after addition of the phenolphthalin reagent.

The reaction is not suitable for the exact colorimetric determination of copper, because the color intensity does not reach a maximum within a reasonable period of time but continually increases with the time of standing. Obviously the test can be used for a rough approximation of the amount of copper present if comparison is made with solution of known copper content, after the same period of standing after addition of the phenolphthalin reagent.

Notes: 1. When attempting to detect less than 0.005 mg of copper p. 1., a blank with redistilled and copper-free water should be carried along with the test to prevent misinterpretation due to possible traces of copper in the reagents. It was found that the supply of distilled water in the laboratory gave a strong test for copper (0.1—0.2 mg p. 1.).

2. The reaction is not quite specific for copper. Substances which have a strong oxidizing action in a medium of ammonia and ammonium chloride oxidize the phenolphthalin in the absence of cyanide and copper. Thus, it was found that ferricyanide, molybdicyanide, hydrogen peroxide, and auric chloride gave a positive test. In order to make the reaction more specific for copper, ammonia, ammonium chloride and the phenolphthalin reagent without cyanide should be added to the solution. If the latter does

not turn pink or red, but does so in the presence of cyanide according to the procedure given above, it may be concluded that copper is present.

3. The possible interference of other metals was investigated by adding various amounts of other metals to a solution containing 0.1 mg. of copper per liter. Silver (0.5 mg. per 10 ml.) did not interfere, and obviously of course zinc in large amounts does not interfere. Small amounts of nickel (0.05 mg. in 10 ml.) did not interfere, but larger amounts (0.5 mg.) slowed up the development of the color, and the color of the nickel solution made the detection of the pink color more difficult. Thallium, bismuth, zinc, lead, cadmium, and mercury in moderate amounts did not interfere. Even larger amounts of mercury do not interfere if enough potassium cyanide is added to dissolve the white precipitate. Traces of ferric iron, cobalt, and manganese (2 mg. per liter) do not interfere but larger amounts should be removed before testing for copper. It is evident from the above that the procedure described is very suitable for the detection of copper in potable waters.

4. The amounts of reagents specified in the procedure were selected after a systematic investigation of the effect of the concentration of each reagent separately.

5. Although of no practical consequence it may be mentioned that the oxidation of phenolphthalin by the cyanide-copper couple was found to be faster in acetic acid medium than in a buffer of ammonia and ammonium chloride.

6. Reduced solutions of eosin and of erythrosin were also used under various conditions instead of phenolphthalin reagent. They did not offer any advantage over the latter.

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Summary: A highly sensitive reaction for copper has been described, based upon the catalytic effect of copper on the oxidation of phenolphthalin in the presence of cyanide in a buffer of ammonia and ammonium chloride. The test is very suitable for the detection of copper in potable waters. The effect of oxygen upon the development of color has been demonstrated.