muir conception, the saturation values become doubtful, tending to show slight increase with further rise in pressure.

5. The data over the whole range of higher pressures are adequately represented by the Langmuir formula.

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TWO DELICATE TESTS FOR THE DETECTION OF COPPER AND SOME REMARKS ON THE RHODANINE TEST OF FEIGL FOR SILVER

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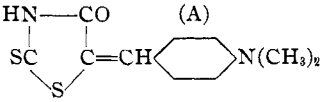

(A)

I. Recently, F. Feigl[1] has described a new and very delicate test for silver with *p*-dimethylaminobenzylidene-rhodanine as a reagent (A). According to Feigl, this reagent gives in weakly acid, neutral and ammoniacal solutions, a flocculent red precipitate with silver. In 5 cc. of a weakly acid solution, one part of silver in 5,000,000 of solvent could be detected. In working with 10 cc. of solution, to which 0.5 cc. of 4 N nitric acid and 0.3 cc. of a saturated solution of the rhodanine[2] in alcohol were added, the same sensitivity was found by the writer. A solution with 1 mg. of silver in a liter produces a distinct reddish brown color (10 cc. of solution, conditions as above); with 0.5 mg. of silver per liter a weakly reddish color was noticed; with 0.2 mg. per liter the solution showed a very weak pink color after ten minutes' standing, distinctly different from the blank, which was slightly yellow. In ammoniacal solution (10 cc. of solution + 1 cc. of 6 N ammonia and 0.1 cc. of indicator) the color in the presence of silver is reddish-brown and in very dilute solutions orange-brown. The sensitivity in this case is about 2 mg. of silver in a liter.

In acid medium the reagent is so sensitive toward silver that it even cannot be used as an indicator for the titration of iodide with silver solution. A weakly acid solution of 0.01 N potassium iodide to which some reagent had been added gave a dark red precipitate after addition of a few drops of 0.01 N silver nitrate. Even the silver in the complex potassium silver cyanide reacts with the rhodanine. According to Feigl, the rhodanine is quite specific for silver. This, however, is not the case, as mercury and copper salts under the right conditions can react with it in a very sensitive

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[1] F. Feigl, *Z. anal. Chem.*, **74**, 380 (1928).

[2] The reagent was prepared in the organic division of this University, according to the procedure given by Feigl. It had the same properties as a sample kindly submitted by Dr. Feigl. Instead of using a 0.03% solution of the rhodanine in acetone as described by Feigl, a saturated solution in alcohol (about 0.02%) was taken.

way. In weakly acid solution (10 cc. + 0.5 cc. of 4 N nitric acid + 0.3 cc. of reagent) mercurous mercury gives a red precipitate; 1 mg. of mercury per liter gives a faintly red color; the limit of sensitivity is 0.5 mg. per liter. Mercurous mercury even reacts in the presence of chloride; therefore, the rhodanine compound must be less soluble than mercurous chloride. Under the same conditions as described for silver and mercurous mercury, the mercuric mercury in well dissociated mercury salts gives a red color (or precipitate) with the reagent; sensitivity, 0.2 mg. of Hg^{II} per liter (in mercuric nitrate). Addition of chloride or bromide decreases the sensitivity very much. A weakly acid solution of 0.1 N mercuric chloride gives a weak pink color the intensity of which depends upon the acidity of the solution. The reaction cannot be used for a sensitive detection of mercuric nitrate in mercuric chloride. The pink color of the mercuric chloride solution becomes gradually stronger on addition of mercuric nitrate or perchlorate (complex $HgCl^+$ formation).

II. Application of the Rhodanine to the Sensitive Detection of Copper.—With cupric salts the rhodanine produces a reddish-orange color; in stronger solutions a precipitate. A solution of 1 mg. of Cu^{II} per liter gives a brown-orange color which is distinctly different from the yellow color of the blank. If comparison is made with a blank, 0.3 mg. of copper per liter can be detected. It should be mentioned that the formation of the colored product is prevented in acid medium. Even acetic acid decreases the sensitivity greatly. On the other hand, if the copper rhodanine is formed in neutral medium (or in the presence of some excess of sodium bicarbonate) it is fairly stable toward acid. An acid cupric copper solution was neutralized with an excess of sodium bicarbonate, then the reagent was added, whereupon it was acidified with acetic acid. The colors become more pronounced in the acid medium (orange-brown). Even 0.5 mg. of Cu^{II} per liter can be detected in 5 cc. of solution if a blank treated in the same way is used for comparison. Lead does not interfere.

Cuprous copper gives much more pronounced colors with the reagent. A weakly acid solution of cuprous copper containing 100 mg. of Cu^{I} per liter gives a purple-violet precipitate; 10 mg., red-brown; 1 mg., orange-brown; sensitivity, 0.1 mg. of Cu^{I} per liter. The rhodanine is very suitable for the detection of traces of copper in a solution. If we start with a cupric copper solution, the divalent ions first must be reduced. This can easily be accomplished with potassium cyanide. To 10 cc. of solution, 3 drops of 1% potassium cyanide and 0.2 cc. of indicator (saturated solution in alcohol) are added and the mixture acidified with acetic acid; sensitivity, 0.3 mg. of copper per liter (comparison with blank). The solution may be acidified with nitric acid instead of acetic acid; 0.5 mg. of copper per liter can be detected easily; the colors fade, however, much sooner than with acetic acid.

Iron interferes with this copper test on account of formation of ferro- or ferricyanide. Therefore, finally, hydrazine sulfate was used as a reagent for the reduction of cupric copper to cuprous copper.

Reagents.—Two per cent. hydrazine sulfate; 0.02% rhodanine in alcohol.

Procedure.—To 10 cc. of the solution add a few drops hydrazine sulfate, sufficient 6 *N* ammonia to give 1 to 2 cc. in excess, 0.2 cc. of rhodanine and acidify, after five minutes' standing, with 30% acetic acid. The cuprous copper reacts even in the ammoniacal medium with the indicator; the color is reddish-violet (100 mg. of copper per liter) or orange-brown (10 mg. and less); sensitivity, 0.5 mg. of copper per liter. The colors are more pronounced after acidifying with acetic acid. Even a solution containing 0.3 mg. of copper per liter gives a distinct red-brown color; sensitivity, 0.1 to 0.2 mg. of copper per liter. The blank shows a yellow to brownish-yellow tinge. In order to reach the maximum sensitivity, it is necessary to let the ammoniacal solution stand for five minutes before adding the acetic acid. The reaction is so extremely sensitive that in all samples of distilled water in the laboratory, the presence of 0.2 to 0.4 mg. of copper per liter could be shown. In the experiments described in this paper, conductivity water or redistilled water from glass vessels was used as a solvent. Water thus obtained gave a negative test for copper. The reaction according to the above procedure is very suitable for the detection of copper in the presence of other cations (silver and mercury excepted). One part of copper in the presence of 2000 parts of lead, bismuth, cadmium, nickel, cobalt and manganese, respectively, could be detected easily. The precipitate formed in the presence of lead or bismuth does not interfere.

Traces of iron do not interfere. Larger amounts can be made harmless by acidifying the ammoniacal solution with phosphoric acid instead of acetic acid. The hydrous ferric oxide goes into solution as colorless complex ferric phosphate. A solution containing 1 mg. of copper and 100 mg. of ferric iron in a liter gave a distinct test for copper. It should be mentioned that the color of the cuprous compound of rhodanine is less stable in phosphoric acid than in acetic acid. It seems that the reaction according to the general procedure is very suitable for the detection of traces of copper in distilled and tap water. The copper content can be approximated by using solutions of known content for comparison.

After this work was finished, an abstract of a paper of O. Funakoshi[3] appeared in *Chemical Abstracts*. It is only stated there that cuprous copper gives a reddish-violet precipitate with rhodanine at about the same sensitivity in neutral or slightly acid solutions. Colors are obtained with concentrated solutions of cupric copper, but the products are much more soluble in water.

III. Recently S. G. Clarke and B. Jones[4] published a note concerning a new and very sensitive reaction for copper. The solution, which must be free from chloride, is neutralized and rendered faintly acid (1 drop of dilute sulfuric acid in excess) and placed in a 100-cc. Nessler glass. One gram of ammonium persulfate is dissolved in the solution; 1 cc. of a saturated alcoholic solution of dimethylglyoxime, 0.5 cc. of 0.5% silver nitrate and 2% of a 10% aqueous solution of pyridine are added and the whole stirred. Copper gives a reddish-violet color. The reaction is quite specific and sensitive to 0.1 mg. of copper in a liter. The author was able to confirm more or less the statements of Clarke and Jones. In working with 10 cc. of solution a sensitivity of 0.3 mg. of copper in a liter was noticed. A serious

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[3] Funakoshi, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **12**, 155 (1929); *C. A.*, **23**, 4644 (1929).

[4] S. G. Clarke and B. Jones, *Analyst*, **54**, 333 (1929).

drawback is that chloride must be absent, which limits the application of the reaction very much. Therefore, it was thought worth while to make a search for another oxidizing agent instead of persulfate. Potassium periodate[5] was found to be very suitable. The high price of this salt is no objection, as for each experiment only 4 mg. of potassium periodate are used. A systematic study showed that the amount of periodate and dimethylglyoxime have a marked influence upon the sensitivity of the reaction. In the presence of much periodate, the red color of the copper compound fades fairly rapidly. The periodate probably oxidizes the glyoxime to some product which gives the red color with copper. An excess of periodate oxidizes this compound further to a colorless product. This could be inferred from the fact that if some dimethylglyoxime was added to a solution which had become colorless on standing, the red color developed again. It would be interesting to know the composition of the compound which gives the red color with copper. If this oxidation product of dimethylglyoxime could be isolated, it might be expected that it would be a valuable reagent for the detection of traces of copper.

Finally, the following procedure was developed for the detection of traces of copper in distilled water.

Reagents.—Saturated solution of potassium periodate in water (0.35 g. of the salt in 100 cc. of water); 0.1% dimethylglyoxime in alcohol (the saturated solution which Clarke and Jones used contains about 1.6 g. of glyoxime in 100 g. of alcohol and is much too concentrated for our purpose). It may be mentioned that an old solution of dimethylglyoxime which had been kept for some years in an ordinary bottle gave a much less sensitive reaction. The reason was that the solution had become strongly alkaline to phenolphthalein.

Procedure.—To 10 cc. of water add 0.2 to 0.3 cc. of 0.1% dimethylglyoxime and 1 cc. of saturated potassium periodate solution. Observe the color after three to five minutes' standing. A violet-red color shows the presence of copper; sensitivity: 0.1 mg. of copper in a liter ($1:10^7$).

Notes.—(1) It makes no difference whether the dimethylglyoxime or the periodate is added first. In order to avoid confusion with nickel, it is advisable to add the dimethylglyoxime first. (2) The red-violet color develops gradually and attains a maximum sensitivity after about five minutes' standing. After long standing, the color fades. Still the procedure described can be applied for the colorimetric determination of traces of copper in distilled water if comparisons are made within fifteen minutes after addition of the reagents. In this way it was found that distilled water in this Laboratory contained 0.2 to 0.4 mg. of copper in a liter. (3) In working with a larger volume than 10 cc., even smaller amounts than 0.1 mg. of copper in a liter can be detected. (4) Small amounts of alkali chlorides and other neutral alkali salts have no influence upon the reaction. Small amounts of sodium bicarbonate (less than 1 g. in a liter) have no influence; with larger amounts the sensitivity decreases somewhat, but even in the presence of 10 g. of sodium bicarbonate per liter, 1 mg. of copper in a liter could be detected easily. (5) Calcium and magnesium, especially in the presence of bicarbonate

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[5] Potassium periodate has been applied for the oxidation of manganese to permanganate. Compare especially H. H. Willard and L. H. Greathouse, THIS JOURNAL, **39**, 2366 (1917).

(tap water) interfere, as they precipitate with the periodate. This difficulty can be overcome by adding to 10 cc. of water 1 cc. of 4 *N* sulfuric acid and 50 mg. of sodium bicarbonate. In this way it could be shown that the Minneapolis tap water contains less than 0.1 mg. of copper in a liter. It is still more convenient to add a buffer solution to the water instead of the combination of sulfuric acid and bicarbonate. The more acid the solution the less sensitive is the reaction. Finally, it was found that with an acetate buffer of P_H 5.8 ± 0.2, good results are obtained.

Acetate Buffer.—One hundred cc. of *N* sodium acetate and 7 cc. of *N* acetic acid.

Procedure.—To 10 cc. of water, 1 cc. of buffer solution is added and then the glyoxime and the periodate as described above; the sensitivity after standing for five minutes is 0.15 mg. of copper in a liter.

The latter procedure can be applied for the detection of copper in tap water if not more than traces of zinc or lead are present; 10 mg. of zinc in a liter has very little influence (color somewhat weaker than in blank without zinc); in the presence of larger amounts of zinc, the latter is precipitated as zinc periodate and the sensitivity decreases very much. The same holds for lead. A solution with 1 mg. of copper in a liter in the presence of 10 mg. of lead per liter gives a distinct reaction though a somewhat weaker color than without lead. Ferric iron also interferes. Still 1 mg. of copper per liter in the presence of 10 mg. of iron per liter gives a distinct reaction. Addition of 1 to 2 drops of *N* disodium phosphate (Na_2HPO_4) before the addition of the buffer gives a great improvement. Under these conditions 1 mg. of copper in the presence of 20 mg. of iron per liter can easily be detected. Other cations such as cadmium, zinc or manganese all interfere, as they precipitate with the periodate. Therefore, the rhodanine reaction is of much more general application than the glyoxime reaction. The latter can only be applied in these cases in which the solution does not contain more than traces of other metal salts.

Summary

1. *p*-Dimethylaminobenzylidene-rhodanine is a sensitive reagent for the detection of mercurous mercury and mercuric ions. Slightly ionized mercuric salts produce only a slight color or none.

2. Salts of cupric copper give an orange-reddish or orange-brown color. The latter is more pronounced in cuprous salts. A delicate and simple test based on this reaction and sensitive to 0.1 mg. of copper in a liter has been described. The reaction is very suitable for the detection of copper in distilled water, tap water and in solutions which contain other metal ions.

3. The reaction of Clarke and Jones for copper, using dimethylglyoxime and persulfate plus silver nitrate, has been modified by using a trace of periodate as an oxidizing agent. The reaction is sensitive to 0.1 mg. of copper in a liter and is very useful for the colorimetric determination of traces of copper in distilled water. A somewhat modified procedure has been described for the detection of copper in tap water. The rhodanine test can be more generally applied than the dimethylglyoxime reaction.

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