

During the process some of the zinc seems to be carried into the crystals, suggesting that the purity of the metal of the crystals increases as it gets further from the center. This is very noticeable in the examples of both gold and copper.

The crystals from these metals differ much in their branching and curving tendencies. In tin, the crystals are straight and the side growths are at right angles. Lead crystals show less tendency to side branching and curve but little. In gold, as well as in some of the other metals, the branching is quite arborescent. Are the crystals of tin an illustration of compounding by relay?

The crystals formed by this method are well represented in the accompanying plates—they are of some scientific interest and form brilliant microscopic objects when viewed by reflected light.

I owe the microphotographs to the kindness of Mr. J. T. Burt-Gerrans, of the University of Toronto. Each small division of the scale corresponds to 0.015 mm. on the slide.

LONDON, ONT.

[CONTRIBUTION FROM THE HARRIMAN RESEARCH LABORATORY, ROOSEVELT HOSPITAL, NEW YORK CITY.]

A NEW TEST FOR COPPER.¹

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Introduction.

The test to be described in this paper is based on the insolubility of the copper salt of α -amino-*n*-caproic acid ($\text{CH}_3(\text{CH}_2)_5\text{CHNH}_2\text{COOH}$). Kudielka,² in 1908, prepared this acid and its copper, nickel and cobalt salts and determined their solubilities in water. In the course of their work on the quantitative determination of amino acids, Kober and Sugiura³ state that the insoluble complex which *n*-aminocaproic acid forms with copper may be useful in analytical work.

Some preliminary work on the part of the authors indicated that an aqueous solution of *n*-aminocaproic acid was an exceedingly valuable reagent for the detection of small amounts of copper. It was the object of this investigation to ascertain the most favorable conditions for the use of this reagent and to determine its applicability to solutions of salts of foreign metals containing small amounts of copper.

The reagent was prepared from commercial *n*-caproic acid by the method proposed by Abderhalden, Fuchs and Froehlich⁴ and further purified

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² *Monatsh.*, 29, 351 (1908).

³ *THIS JOURNAL*, 35, 1584 (1913).

⁴ *Z. physik. Chem.*, 86, 455 (1913).

through its copper salt. The solution used throughout our work was prepared by dissolving 0.67 g. of the acid in 100 cc. of water; the mixture was heated to facilitate solution and then filtered.

It was found that the precipitation of copper by aminocaproic acid was influenced considerably by the presence of free mineral acid. Since mineral acid is liberated as a by-product of the reaction, it was decided to employ a buffer in making the test. For this purpose a 40% solution of sodium acetate was found satisfactory.

The pure copper salt of *n*-aminocaproic acid was prepared. Evaporation of 1000 cc. portions of an aqueous solution of this compound gave residues from which the solubility of the salt at 18° was calculated to be of the order of 1 in 100,000.¹

Determination of the Sensitiveness of the Test.—By means of a graduated pipet definite amounts of a standard copper nitrate solution were introduced into a series of test tubes. 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid solution were then added, the contents of the tubes shaken and allowed to stand. The results obtained are shown in Table I.

TABLE I.

No.	Mg. Cu.	Result.
1.....	1.000	Immediate grayish blue precipitate.
2.....	0.500	Immediate grayish blue precipitate.
3.....	0.010	Slight white precipitate.
4.....	0.005	Faint precipitate at end of 5 minutes.
5.....	0.004	Fair test in 5 min.; much better in 12 minutes.
6.....	0.003	Faint test in 5 min.; (limit) much better in 12 min.
7.....	0.002	Negative test in 5 min.; faintly positive in 12 min.
8.....	0.001	Negative test in 12 min.
9.....	0.000	Negative test in 12 min.

Comments.—The above experiments were repeated a number of times with the same results. The limit of the test in 5 minutes (0.003 mg. Cu in 1 cc. of the original solution) represents a concentration of 1 part in 333,000. While it requires some practice to recognize the test given by 0.003 mg. of copper, decided and unmistakable results are obtained with 0.004 mg. The precipitate has a tendency to agglutinate, to rise to the surface of the liquid and to creep up the walls of the tube when the latter is gently shaken. This characteristic property of crawling up the sides of the containing vessel makes possible the recognition of smaller amounts of precipitate than would be the case if the precipitate remained in suspension or settled to the bottom of the container. The "crawl" is best seen by gently shaking the tube and viewing it in good light against a

¹ Kudielka (*Loc. cit.*) found the solubility of the copper salt to be 3.6 parts in 100,000 at 23°.

dark background. In some of the preliminary tests with 0.004 mg. Cu, negative results were obtained. An examination into the causes showed that the greasy condition of the tubes prevented the precipitate from crawling. It is therefore imperative in making the test to have the tubes scrupulously clean. This was accomplished by first scrubbing with soap solution, rinsing, then treating with hot chromic acid mixture and finally rinsing a number of times with distilled water. The solutions to be tested for copper were always carefully examined for any particles in suspension that might be mistaken for a positive test and if not absolutely clear, the solution was filtered before adding the reagent.

A comparison of the sensitivity towards copper of *n*-aminocaproic acid and synthetic leucine was then made. A solution of Kahlbaum's synthetic leucine of the same strength as our reagent (0.67%), failed to give a precipitate with amounts of copper smaller than 0.03 mg. Thus the normal acid will detect about one-tenth the quantity of copper that can be recognized with the iso-derivative. The presence of moderate amounts of the iso-derivative was found to materially diminish the sensitivity of the reagent.

Behavior of the Reagent with Other Metals.—Having determined the limit of the test in solutions containing copper alone, our next step was to ascertain whether there were any other metals which would give the test. To this end, 1 cc. of a solution containing 100 mg. of the metal as nitrate or chloride was treated with 1 cc. of 40% sodium acetate solution and 1 cc. of aminocaproic acid. *Of all the common metals, zinc and mercury alone gave precipitates.* The test given by zinc under these conditions was very faint, but by diminishing the quantity of zinc to a few milligrams, surprisingly strong reactions were obtained.

This anomalous behavior of zinc salts necessitated a repetition of the above experiments with small quantities (1–10 mg.) of each of the metals. The results showed that mercury and zinc alone gave precipitates and therefore interfere with the test for copper. Methods for overcoming these interferences were devised and will be given later when these metals are considered.

Whether or not the presence of large amounts of foreign metals would interfere with the detection of relatively minute quantities of copper was the next point investigated. The general procedure was as follows:

To 1 cc. of the solution containing 100 mg.¹ of the foreign metal, 0.1 cc. of copper nitrate solution containing 0.01 mg. of Cu was added. To this mixture, 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid were added. A control was run at the same time and in every case the results were checked by repeating the experiment. Following this pro-

¹ Because of the relatively small solubility of AlCl_3 , 2 cc. of solution were required to supply 100 mg. of Al.

cedure, good tests were obtained in the presence of Pb, Cd, Ni, Co, Mn, Ba, Sr, Ca and Mg, respectively. With lead solutions, a finely divided precipitate appeared in the controls at the end of 10 minutes, though they were perfectly clear at the end of 5 minutes. For this reason it was decided to remove the greater part of the lead with 1 cc. of 20% NaCl solution. After washing the precipitated lead chloride with 1 cc. of cold water, good tests and perfect controls were obtained.

Interferences.—It was thought that substances which form only slightly ionizable complexes with copper would interfere with its precipitation by aminocaproic acid. Experiments showed that an excess of KCN inhibits the test. In Table II the influence of ammonium salts is shown.

TABLE II.

Total Volume, 3 cc.; 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$; 1 cc. of the Reagent.

No.	Mg. Cu.		Result.
1-2.....	0.004	0.6 cc. 50% NH_4NO_3	Negative in 10 hours.
3-4.....	0.004	0.6 cc. 30% NH_4Cl	Negative in 10 hours.
5-6.....	0.004		Good test in 5 minutes.

Smaller amounts of ammonium salts were found to retard the formation of a precipitate. Substances containing amino groups were also found to interfere. Thus negative tests for 0.01 mg. Cu were obtained in the presence of 10 mg. of each of the following substances: Glycocoll, synthetic leucine, glycylic acid, "Seiden peptone" and casein.

Sodium citrate was also found to interfere; but contrary to expectations good tests were obtained with 0.004 mg. Cu in the presence of relatively large amounts of tartrates.

The interference due to ammonium salts and organic matter may readily be removed by ignition.

Special Procedures.

Silver.—The addition of 1 cc. 40% sodium acetate solution to 1 cc. of a 10% Ag solution causes the precipitation of silver acetate. In the absence of sodium acetate, a test was not obtained with 0.01 mg. Cu in the presence of 1 cc. of 10% silver solution. It was therefore necessary to remove the silver before the test could be applied. This was accomplished by means of sodium chloride. The results of the experiments appear in Table III.

TABLE III.

Total Volume before Precipitating with 1 cc. 20% NaCl, 1.1 cc. To Filtrate Added
1 cc. 40% $\text{NaC}_2\text{H}_3\text{O}_2$, 1 cc. Reagent.

No.	Mg. Ag.	Cu.	Result.
1-2.....	100	0.00	Negative
3-4.....	100	0.01	Good

Bismuth.—A solution of $\text{Bi}(\text{NO}_3)_3$ in 10% conc. HNO_3 containing 100 mg. of the metal per cc. was used. One cubic centimeter of this

solution was found to be too acid to yield a precipitate in the presence of copper. The procedure which gave satisfactory results was as follows:

To 1 cc. of the bismuth solution 0.01 mg. of copper was added. The solution was then diluted to 20 cc. This caused a separation of basic salt. After standing for several minutes, 2 cc. NH_4OH (1-1) were added drop by drop and the mixture was filtered. The filtrate and washings were evaporated to a few drops,¹ taken up with water, filtered again through a very small filter and then treated with 1 cc. of sodium acetate and 1 cc. of the reagent. Good results were obtained in 5 minutes.

Antimony.—A 10% solution of antimony as chloride was used. The method employed was similar to that described above for bismuth. Good tests and controls were obtained.

Tin.—A solution of SnCl_4 containing 100 mg. Sn in 1 cc. was employed in all our tests with this metal. 1 cc. of this solution yields a precipitate when treated with 1 cc. of 40% sodium acetate. By precipitating the tin with NH_4OH or 40% $\text{NaC}_2\text{H}_3\text{O}_2$, nearly all the copper originally added either combined with, or was adsorbed by, the precipitate. This was shown by the blue color of the precipitate. We were unable, moreover, after repeatedly washing the precipitate with either water, or dilute NH_4OH , to get a test for copper in the combined filtrate and washings after concentration to 0.5 cc. when less than 0.1 mg. of Cu was originally present. By removing the ammonium salts from the filtrate, the test was rendered more delicate, but 0.02 mg. of copper always escaped detection. As nickel does not interfere with the test, it was thought that by adding a small amount of this metal (2-10 mg.) to the solution of copper and tin, it would be possible by means of an excess of potassium hydroxide to precipitate the copper with the nickel and thus keep all the tin in solution. This procedure, however, failed to detect 0.05 mg. of copper for the reason that the precipitated nickel adsorbed some tin which could not be washed out and which interfered with the final test. Based on the volatility of stannic chloride in hydrochloric acid solution, a method was found which yielded uniformly satisfactory results. The solution containing the tin and copper was treated with HCl and evaporated *just to dryness*: more HCl was then added and the solution again evaporated. After the third evaporation, 1 cc. of water was added and the solution treated with 1 cc. of 40% $\text{NaC}_2\text{H}_3\text{O}_2$ and 1 cc. of the reagent. The results are shown in Table IV.

TABLE IV.

No.	Mg. Sn.	Mg. Cu.	Result.
1.....	100	0.100	Strong test.
2.....	100	0.010	Strong test.
3.....	100	0.006	Good.
4-5.....	100	0.000	Negative.

¹ By removing the ammonium salts at this point, better results may be obtained.

Zinc.—Table V gives the results obtained with solutions of zinc of strength 100 mg. in 1 cc.

TABLE V.

Volume before the Addition of Reagent, 1.1 cc.; 1 cc. of 40% $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$; 1 cc. of Reagent.

No.	Mg. Zn.	Mg. Cu.	Results.
1-2.....	100 as $\text{Zn}(\text{NO}_3)_2$	0.01	Precipitate.
3.....	100 as $\text{Zn}(\text{NO}_3)_2$	0.00	Precipitate.
4.....	100 as ZnSO_4	0.00	Precipitate.
5-6.....	200 as ZnSO_4	0.10	Immediate precipitate.
7-8.....	200 as ZnSO_4	0.00	Negative in 1 hour.

These results find their explanation in the acidity contributed by the zinc salt. 200 mg. of Zn gave a higher hydrogen ion concentration to the solution than that given by 100 mg. and as a consequence no precipitate was obtained in Experiments 7 and 8. If this explanation be correct, 1 mg. of Zn should give a better test than 100 mg. Experiments showed not only that this was the case, but also that *n*-aminocaproic acid is a fairly sensitive reagent for the detection of small amounts of zinc as shown in Table VI.

TABLE VI.

Solution ZnSO_4 . 1 cc.; 1 cc. of 40% $\text{Na}_2\text{C}_2\text{H}_3\text{O}_2$; 1 cc. of Reagent.

No.	Mg. Zn.	Result.		
		1 min.	2 min.	5 min.
1.....	0.05	Good.	Strong.	Strong.
2.....	0.03	Negative.	Good.	Very good.
3.....	0.02	Negative.	Negative.	Very faint (limit).
4-5.....	0.01	Negative.	Negative.	Negative.

The results in Table VI show that under the conditions employed in testing for copper, the reagent is capable of detecting 0.02 mg. of zinc. Since the reagent is sensitive to small quantities of zinc, there was need for a means of differentiating between zinc and copper if the test were to be applied to unknown solutions. After some experimentation, it was found that zinc does not precipitate when the hydrogen ion concentration (*p*-nitrophenol as indicator) exceeds $10^{-5.5}$. If to an acid solution of zinc containing aminocaproic acid and a drop of *p*-nitrophenol solution (0.04%), sodium acetate be added, a yellow color will develop which deepens on further addition of acetate. When the color is only a faint yellow, ($C_{\text{H}^+} = 10^{-5.2}$) no zinc will come down. Not until sufficient sodium acetate has been added to give a strong yellow color ($C_{\text{H}^+} = 10^{-5.8}$) will the zinc precipitate in 5 minutes. The results in Table VII show the reliability of the method.

TABLE VII.

Volume, 2 cc.; One Drop *p*-Nitrophenol; Adjusted to Light Yellow Color with Sodium Acetate and 0.1 N HCl; 1 cc. Reagent.

No.	Mg. Zn.	Mg. Cu.	Result.
1-5.....	1.0	0.000	Negative in 5 minutes.
6-10.....	1.0	0.004	Positive in 5 minutes.

Mercury.—The following solutions were used in the experiments with mercury, *viz.*: Solution A, Hg 10% (as nitrate) in 2% conc. HNO₃; Solution B, Hg 10% (as chloride) in 5% NaCl solution;¹ Solution C, Hg 1% (as chloride) in H₂O.

1 cc. each of solutions A, B and C was treated with 1 cc. of 40% NaC₂H₃O₂ and 1 cc. of the reagent. A fair test was obtained with solution A, B was negative, while solution C gave a strong test.

These results indicated that the presence of NaCl prevented the precipitation of the mercury. To further test this conclusion the following experiments were made:

TABLE VIII.

Volume after the Addition of 1 cc. of 40% NaC₂H₃O₂, 3 cc.; 1 cc. of the Reagent.

No.	Mg. Hg. (Sol. A).	Mg. Cu.	20% NaCl cc. ²	Result.	
				5 min.	10 min.
1.....	100	0.00	0.0	+	+
2-5.....	100	0.00	1.0-0.5	—	—
6-8.....	100	0.01	1.0-0.5	+	+
9.....	1	0.00	0.0	Immediate heavy ppt.	
10-11.....	1	0.00	0.5-0.1	Negative.	

TABLE IX.

Experiments with HgCl₂ solutions. 1 cc. 40% NaC₂H₃O₂; 1 cc. Reagent.³

No.	Mg. Hg. (Sol. B).	Mg. Cu.	20% NaCl cc.	Result.
1-2.....	100	0.00	0.0	—
3-4.....	100	0.01	0.0	+
5 ⁴	1	0.00	0.0	Immediate heavy ppt.
6 ⁵	1	0.00	0.5	Negative in 10 min.
7 ⁵	1	0.00	0.1	Negative in 10 min.

The results of the table show that the addition of NaCl will prevent the formation of basic salt or aminocaproate in solutions of mercury. Before concluding our work with this metal we determined that small amounts may also be prevented from precipitating by regulating the acidity as in the case of zinc.

Iron and Aluminum.—In the presence of 100 mg. of either of these metals in the form of chlorides, we were unable to get positive tests with

¹ The NaCl was added to increase the solubility of HgCl₂.

² The addition of NaCl to the Hg solution causes the formation of an exceedingly faint cloud, due probably to HgCl₂ in suspension. The solution clears up somewhat on the addition of the aminocaproic acid. However, in no case was this cloud found to interfere with the test. In the many experiments made, the controls never showed the characteristic "crawl;" while in the presence of copper decided tests were obtained.

³ In tests 1-4 the volume of the solution before the addition of the reagent was 2 cc.

⁴ In tests 5-7 the volume of the solution before the addition of the salt was 1 cc.

⁵ At the end of 10 minutes, 9 mg. of Hg were added slowly from a pipet to these tubes. No precipitate formed in 10 minutes.

0.05 mg. of copper or less. This is due to the fact that before the acidity can be depressed sufficiently to permit the precipitation of small amount of copper (C_{H^+} about 10^{-4}) these metals (also Cr) separate in the form of hydroxides and mask the reaction. After much experimenting the following procedure was found efficient: 100 mg. of Fe or Al in the form of their chlorides were mixed with 0.05 mg. Cu as nitrate. The mixture, the volume of which was about 2 cc., was slowly poured with constant stirring into 3 cc. NH_4OH (1-1); the solution was filtered through a fluted filter and the precipitate washed with 2 cc. of water. The combined filtrate and washings were evaporated to dryness and the ammonium salts removed by heating with KOH. The solution was then made acid with HCl, evaporated to one drop, taken up with 1 cc. of water, and tested in the usual manner. By this procedure good tests were consistently obtained in 3 minutes.

Chromium.—A 10% solution of Cr as $Cr(NO_3)_3$ was used in this work. 1 cc. of this solution to which 0.05 mg. of copper were added failed to give the test. Precipitation with NH_4OH , as in the procedure for Fe and Al, did not serve in this case, owing to the appreciable solubility of $Cr(OH)_3$ in ammonia. The filtrate always contained sufficient chromium to confuse the test.

To determine whether the oxidation of the chromium to chromic acid would eliminate the interference of this metal, tests were made for copper in the presence of K_2CrO_4 . The results showed that 100 mg. of Cr as chromate did not prevent the precipitation of 0.01 mg. of Cu. Subsequent experiments, however, starting with the metal as nitrate and oxidizing to chromate with sodium peroxide did not give consistent results.

After oxidation it was necessary to make the mixture acid in order to keep the copper in solution. In this connection a difficulty was encountered in attempts to adjust the acidity; for the test, even when 1 cc. of 40% sodium acetate is used, cannot be applied if the initial acidity is too great. Again, the strong color of the chromate solution does not permit the use of the indicator, without which it would be impossible in an unknown solution to determine whether the test were due to the presence of copper or zinc. It was, therefore, necessary to remove the CrO_4 . The chromate was dissolved in about 10 cc. of water, 1 cc. of NH_4OH (1-1) added, the mixture heated to boiling and an excess of $BaCl_2$ added. This procedure appeared sound, first because the presence of barium would not interfere with the test, and second, because $BaCrO_4$, being crystalline, would not adsorb appreciable quantities of copper. The filtrate from the $BaCrO_4$ was evaporated just to dryness, taken up with 1 cc. of water and refiltered through a very small filter into a test tube. 1 drop of *p*-nitrophenol was then added, the acidity adjusted to a faint yellow and 1 cc. of the reagent added. The following results were obtained:

No.	Mg. Cr as K ₂ CrO ₄ .	Mg. Cu.	Mg. Zn.	Results.
1.....	100	0.05	0.0	Good test in 1 min.
2.....	100	0.00	0.1	Negative test in 5 min.

At the expiration of 5 minutes the contents of Tube 2 were divided into two portions. 0.02 mg. of Cu added to one portion gave a good test, showing that the conditions were favorable for the precipitation of copper. To the other portion 0.1 *N* NaOH was added till a strong yellow color developed. A copious precipitate was then obtained, showing the presence of zinc.

Nickel and Cobalt.—The reagent is capable of detecting 0.01 mg. of copper in the presence of 100 mg. of either of these metals.¹ Although the aminocaproates of nickel and cobalt are fairly insoluble,² these salts are not formed under ordinary conditions when $C_{H^+} > 10^{-7}$. Thus they are much more sensitive to acid than the corresponding zinc salt and, consequently, conditions permitting the differentiation between copper and zinc will completely prevent the precipitation of nickel and cobalt. Although the results showed that under our conditions (1 cc. 40% sodium acetate³ as buffer) nickel and cobalt remained in solution, a small decrease in the hydrogen ion concentration, such as might be caused by a trace of alkali in the sodium acetate or by heating the mixture, would bring about a slight precipitation of these metals. Consequently, in an unknown solution, when 1 cc. of 40% sodium acetate is used as a buffer, a positive test cannot be regarded as conclusive for copper, because of the possible presence not only of zinc but also of nickel and cobalt. The strong color of solutions of nickel and cobalt precludes the use of *p*-nitrophenol as an indicator for adjusting the acidity. We know of no feasible method whereby a separation of 0.01 mg. of copper from 100 mg. of nickel or cobalt can be effected. We therefore recommend in such cases the following procedure. To the neutral or faintly acid solution add 1 cc. of 40% sodium acetate and 1 cc. of aminocaproic acid. Allow the mixture to stand for about one-half hour.⁴ The precipitate, which may consist of aminocaproates of Cu, Zn, and traces of Ni and Co, is collected on a small filter, thoroughly washed, and then dissolved in hot dilute HCl. The filter is well washed, the combined solution and washings concentrated, *p*-nitrophenol added, the acidity adjusted to a pale yellow, and finally 1 cc. of aminocaproic acid added. A precipitate proves the presence of copper. Following this procedure, good tests were obtained

¹ With some preparations of the nitrates of nickel and cobalt, only very faint tests were obtained in 5 minutes; on standing for 10 or 15 minutes, however, the tests improved decidedly.

² According to Kudielka (*Ibid.*), the solubility of the nickel salt is about 29 parts in 100,000; that of the cobalt salt is 21 parts in 100,000.

³ Kahlbaum's zur Analyse.

⁴ This is to insure complete precipitation; frequent agitation is advantageous.

from solutions containing 0.02 mg. of copper and 50 mg. of nickel or cobalt in a volume of 1 cc. In the absence of copper, this method gave good controls.

Procedure for Unknowns Containing all Metals.—We do not know of a systematic procedure whereby any of the sensitive reagents hitherto employed for the detection of minute amounts of copper can be applied to solutions containing all the common metals. The great difficulty encountered in such cases is to be found in the tendency of precipitates, particularly those of a gelatinous character, to adsorb appreciable quantities of copper. Based on our experience with the test when applied to the metals individually, we would suggest the following procedure, observing the precautions necessary in quantitative work. After the removal of the silver group by means of HCl, the filtrate and washings are treated with an excess of KOH, heated and filtered. The precipitate is then dissolved in HCl and evaporated to a few drops. More HCl is added and the solution again evaporated to a few drops. The diluted solution is then poured into an excess of NH₄OH and filtered. The filtrate is evaporated to dryness and boiled with KOH to remove ammonium salts. The solution is then acidified with HCl and heated to dissolve the CuO.¹ 1 drop of *p*-nitrophenol is added, the acidity adjusted and test applied.

Remarks Concerning the Comparative Merits of the Reagents for Copper.—*N*-Aminocaproic acid possesses an important advantage over all the other reagents used for the detection of small amounts of copper in that, when the simple precautions to avoid the interference of zinc or mercury are taken, the test is highly characteristic and specific for copper.

It appears to be more delicate than the ammonia test according to the figures given by Pritz, Guillanden and Withrow,² and it possesses the further advantage that the interference of nickel may be readily overcome. Experiments with 0.004 mg. of copper gave decided tests with *n*-aminocaproic acid, but with ferrocyanide the tests were not evident except when compared with the blank; moreover, with ferrocyanide, the color, even with considerable amounts of copper, could not be distinguished from that of the control when examined at night. Again with the ferrocyanide test there are many more metals which interfere than is the case with aminocaproic acid. Solutions containing amounts of Fe, Ni, Co, Pb, Cd, Mn small enough to permit the use of an indicator may be tested directly with aminocaproic acid. Thus the almost universal presence of traces of iron, which would prevent the direct use of the ferrocyanide test, will

¹ If the solution is colored, and the indicator cannot be satisfactorily employed, recourse must be had to the procedure recommended for Ni and Co.

² THIS JOURNAL, 35, 168 (1913).

not interfere in the least with the aminocaproic acid test. Ammonium sulfide has¹ also been recently shown to be an exceedingly sensitive reagent for copper, but the large number of metals which interfere materially limits its usefulness. At the present time the cost of *n*-aminocaproic acid greatly exceeds that of the other reagents, but it is believed that its great usefulness will serve to cheapen it considerably. It is moreover a simple matter to recover the acid from waste solutions; so that the same supply can be used repeatedly.

Experiments are now in progress in this laboratory to determine the behavior of the rarer elements with *n*-aminocaproic acid and also the conditions under which the reagent may be applied as a specific test for zinc. The use of this reagent for the purposes of quantitative analysis is also under consideration.

Summary.

1. It has been shown that an aqueous solution of normal aminocaproic acid is an exceedingly sensitive reagent for the detection of copper. With this reagent 0.004 mg. of copper may be detected with certainty.

2. Mercury and zinc are the only other common metals which yield, under the conditions specified, a precipitate with the reagent. The interference of the former may be overcome by the addition of sodium chloride, the latter may be prevented from precipitating by adjusting the acidity of the solution.

3. Procedures have been given for the detection of small amounts of copper in the presence of relatively large quantities of foreign metals.

4. The reagent is more specific for copper than any of the other reagents heretofore proposed; and possesses an advantage over the ferrocyanide test in that small quantities of iron do not interfere with its use.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN.]

PERMANGANATE DETERMINATION OF IRON IN THE PRESENCE OF FLUORIDES—THE ANALYSIS OF SILICATES AND CARBONATES FOR THEIR FERROUS IRON CONTENT.²

By O. L. BARNEBY.

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The permanganate titration of ferrous iron in the presence of chlorides has attracted attention for a considerable period of time because of the economic importance of the determination of iron, the ease with which iron ores dissolve in hydrochloric acid and the rapidity of conducting the permanganate titration. While the titration of iron with permanganate in hydrochloric acid solution has been studied by many inves-

¹ THIS JOURNAL, 35, 168 (1913).

² Read at the New Orleans Meeting of the American Chemical Society.