when low humidity usually prevails indoors, and at such times the difference in temperature between the water and the surrounding atmosphere may amount to 4° or more. It takes some time for the sample to attain the temperature of the water, if it is drawn directly into the buret, and if accurate results are to be obtained with the original Pettersson-Palmqvist apparatus or with any of the forms mentioned under group II, the manipulation cannot be continued until this condition has been satisfied. In many cases the movement of the manometer liquid resulting from the change of volume due to this cause alone is greater than would result from the removal of the carbon dioxide that the sample contains. The necessity for delay is completely obviated when the sample is drawn through the copper coil.

The apparatus is manufactured by Greiner and Friedrichs, Stützerbach in Thüringen, Germany.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY.]

THE DETECTION OF TRACES OF COPPER.[1]

BY WESLEY B. PRITZ, A. GUILLAUDEU AND JAMES R. WITHROW.

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A frequent feeling of uncertainty regarding the significance of qualitative tests for the completeness of the electrolytic precipitation of copper, made it desirable to know the limits of the sensitiveness of the recommended reagents, as commonly employed. It was also desired to modify, if necessary,. the sensitiveness of one of the reagents to meet the requirements of the work on electrolytic precipitation of copper in progress in this laboratory. As it is often essential in electro-analysis to remove only such volume of solution for the qualitative test as will contain an insignificant weight of copper, the method selected must be made applicable to samples not greater than about one cc. Of the reagents recommended, the ones which in our experience are in most general use are ammonium hydroxide, ammonium sulfide and potassium ferrocyanide. Since a study of the sensitiveness of these three, under the conditions in the copper work on hand, showed that ferrocyanide could be made to answer our purpose, other methods were not examined.

Heine[2] appears to have utilized color for the detection of copper as early as 1830. Müller, in 1855,[3] with his complement colorimeter using 5 cc. of solution was able to detect 50 parts of copper in one million, using ammonium hydroxide as reagent. Wagner, in 1881,[4] stated that the

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[1] Read before the Indianapolis meeting of the American Chemical Society.

[2] Heine, *Bergwerksfreund*, 1, 33; 17, 405; *Z. anal. Chem.*, 46, 644.

[3] *J. prakt. Chem.*, 66, 203.

[4] *Z. anal. Chem.*, 20, 351.

blue color given to solutions of copper salts by ammonium hydroxide will detect one part in 25,000. Milbauer and Stänek, in 1907,[1] thoroughly investigated this color and found that free ammonia and ammonium chloride diminished the intensity, but ammonium carbonate intensified it one-third.

Carnelley, in 1875,[2] found that in acid solution, ferrocyanide will detect one part of copper in 1,000,000 parts of water, while in neutral solution the color changes from brown to purple brown and one part copper can be detected in 1,500,000 parts. The addition of ammonium nitrate or any other ammonium salt greatly increases the depth of color, making possible the detection of one part of copper in 2,500,000 parts. Hydrogen sulfide is also said to detect one part of copper in 2,500,000 parts of water. Wagner, in 1881,[3] reported that ferrocyanide will detect one part of copper in 200,000 parts of solution. Nessler and Barth, in 1883,[4] used 10 cc. of solution and could detect two parts in 1,000,000 with the use of potassium ferrocyanide. Cooper, in 1886,[5] by using varying depths of solution up to fourteen and one-half inches in tubes inclosed in opaque cylinders, claims ability to detect one part of copper in 1,950,000 parts of water with ammonium hydroxide and one part in 11,750,000 parts with ferrocyanide. H. Thoms, in 1894,[6] placed the limit of this last test at one part in 200,000. Bradley, in 1906,[7] found that potassium ferrocyanide could detect copper in a solution containing one part in 100,000, but not in a solution of one part per million.

Such variation in values for the sensitiveness of the reagents mentioned should surely meet any requirement which might arise. We made no attempt to reconcile or judge between any of them, except insofar as our own conditions were concerned. Many other tests have been advanced from time to time and doubtless have much value in their place. The range of recommendation even in this kind of work is quite broad, but from our point of view somewhat lax. Such tests as raising the level to see if fresh copper is deposited[8] and electrolyzing until the solution becomes colorless,[9] do very well in many cases, but frequently are inadequate. We have noticed, for instance, in cases where

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[1] *Z. anal. Chem.*, **46**, 644.

[2] *Chem. News*, **32**, 308.

[3] *Z. anal. Chem.*, **20**, 349.

[4] *Ibid.*, **22**, 37.

[5] *J. Soc. Chem. Ind.*, **5**, 84.

[6] *Pharm. Centralhalle*, **31**, 31; *Z. anal. Chem.*, **33**, 464.

[7] *Chem. News*, **94**, 189.

[8] "Analytical Chemistry," Treadwell-Hall, Vol. II, p. 148 (1905); "Quantitative Chemical Analysis," Fresenius-Cohn, 621 (1908); "Technical Methods of Ore Analysis," Low, 89 (1908); "Quantitative Chemical Analysis," Julian, 250; Warwick, *Z. anorg. Chem.*, **1**, 289.

[9] Rudörff, *Ber.*, **21**, 3050.

the test used was the raising of the level of the electrolyte toward the end of a precipitation between insoluble electrodes and no visible copper was deposited, that there was a sensible lowering of the intensity of the ferrocyanide test made before and then after the rise in level.

Experimental.—The stock solutions used contained one part of copper as sulfate in 1000 and also in 25,000 parts. The copper sulfate was "Baker's Analyzed" in the last case and iron-free crystals recrystallized after several precipitations as crystal meal in the other case. In the preliminary experiments, when 1 cc. portions of solution were examined in ordinary test tubes, the conservative statements in the literature regarding sensibility were confirmed, although somewhat greater sensitiveness could be obtained. In the case of ammonium hydroxide one part of copper in 40,000 could be detected, but not with as great certainty as 1 in 25,000. With potassium ferrocyanide in presence of acetic acid the sensitiveness varied roughly inversely as the concentration of the ferrocyanide solution used. One drop of 8.5% ferrocyanide added to 5 cc. of solution in an ordinary test tube could detect one part of copper in 200,000 parts of solution, but not in 300,000 parts. A 3% solution of ferrocyanide added in the same way to 1 cc. portions gave a distinct pink, with a dilution of one part in 300,000 and not with one in 600,000. The same results were obtained using 2 cc. portions. These results were not as delicate as desired. It was found, too, that slight variations in the procedure when making and examining the tests gave pronounced differences in results. This doubtless has a bearing on the widely varying values on record. In fact, a study of the literature seems to indicate that a major factor in the variations in the recorded values is the lack of uniformity in the quantity of sample used. In our work means of regulating other factors causing difficulty were developed.

Apparatus.—The apparatus finally adopted for detecting traces of copper was an adaptation of the ordinary Nessler tube and was exceedingly simple. A number of tubes were made, 3 to 5 mm. in internal diameter and up to 15 cm. in length, having a capacity of nearly 3 cc. They were made from ordinary thin-walled glass tubing, one end being sealed and preferably slightly ballooned to avoid thickening. The glass used was the lightest obtainable. When viewed on the end it must not be green, or the delicacy of the tests will be affected. The side walls of the tubes were wrapped with black paper to exclude all light except that entering the bottom of the tube. This wrapping greatly increased the delicacy of the tests on the weaker solutions. The solution to be tested was introduced into the tube by means of a 1 cc. pipet.

Ammonium Hydroxide Reagent.—Three drops of this reagent (sp. gr. 0.904) were added to the 1 cc. of solution to be tested, contained in a tube. A blank containing 1 cc. of distilled water and three drops of the hydroxide was also prepared in each case. The two tubes were observed in light thrown up through them from a white screen. $N/2500$ copper sulfate solution gave an easily distinguishable coloration; with $N/3000$ the color was faintly distinguishable, while with $N/4000$ it could scarcely be distinguished at all. $N/3000$ was, therefore, taken as the limit of the sensibility of ammonium hydroxide in the detection of copper in sulfate solutions in such tubes as described. This means that in 1 cc. of electrolyte tested copper may still be detected with the ammonium hydroxide reagent when the electrolyte contains 0.00106 g. of copper per 100 cc. or 10.6 parts per million. This is too much copper to leave in the electrolyte when a gram or less of copper is being deposited.

Ammonium Sulfide Reagent.—This reagent was made in the usual manner and used as the ammonium hydroxide just described. Solutions as dilute as $N/20{,}000$ gave evidence of the presence of copper. The color from $N/25{,}000$ solutions could scarcely be differentiated from that of the blank comparison tube. $N/20{,}000$ was, therefore, established as the practical limit of sensibility with ammonium sulfide. This means 0.00016 gram copper per 100 cc. of solution when 1 cc. of the solution is used in the test, or 1.6 parts per million. This sensibility was in close agreement with the error in weighing of the work under way and would therefore have been satisfactory had it not been found that the reagent must practically be made fresh on the day it is used or the results are not dependable. The reagent decreases in sensitiveness. After six days' standing in a stoppered bottle, in one case, the reagent failed to detect any copper in an $N/5000$ solution. One week later copper could scarcely be detected in an $N/1000$ solution, with the original reagent. The addition of ammonium hydroxide to reduce the yellow color assumed by the deteriorated ammonium sulfide reagent did not seem to improve its sensibility. The work on ferrocyanide resulted so satisfactorily that the ammonium sulfide deterioration was not further investigated.

Potassium Ferrocyanide Reagent.—This reagent gave the best satisfaction. It is in quite common use, but is frequently erroneously thought to be entirely too delicate. It was prepared by dissolving one gram of Baker's C. P. ferrocyanide in 50 cc. of water. This was amply strong to precipitate the copper and not so colored as to interfere greatly with the delicacy of the test. A pinkish brown color was obtained with the dilutions of copper salt used. Three drops of the reagent were used, and the tests conducted as described above. The copper in $N/20{,}000$ solution could easily be detected by this reagent but the color difference became less and less marked as dilution took place. At a dilution of $N/35{,}000$ the color difference (compared with the blank) was just discernable. This was, therefore, the limiting sensibility, and indicates the presence of 0.00009 gram of copper in 100 cc. when 1 cc. is used in the test, or 0.91

parts per million. This is not quite twice as delicate as the test with fresh ammonium sulfide. It is much more delicate than when the test is performed with a drop of the solution on white porcelain, even when the ferrocyanide is as dilute as 0.1 %.

Influence of Reagents.—The influence of the proportions of the reagent and its auxiliaries as well as other substances was studied in the case of potassium ferrocyanide by means of Nessler tubes in 50 cc. portions. The tubes were wrapped with black paper. Difficulty was at first experienced in using the ferrocyanide test on samples from a nitric acid electrolyte. This was caused by a yellowish green coloration which formed in the tube containing the electrolyte, masking any pink color which might be produced. Sometimes the pink which appeared was at once superseded by the green color. The interfering color did not seem to appear in samples containing a negligible amount of copper (0.1 mg. or less in 125 cc.). The addition of 2% of nitric acid to the ferrocyanide-copper nitrate mixture produced cloudiness, interfering with the delicacy of the test. Acetic acid on the other hand did not interfere and really produced a better coloration. Ammonium hydroxide seemed to destroy the copper ferrocyanide color and gave a colorless to green color when in excess. The addition of an acid brought this color out again. An excess of potassium ferrocyanide affects the delicacy of the test in that it changes from pink to yellow, thereby slightly decreasing the delicacy. Ammonium nitrate increases the delicacy of the test. Excess of acetic acid is of little influence. Ammonium acetate has no effect.

Interference of Other Metals.—Zinc has no effect on the delicacy of the ammonium hydroxide reagent when sufficient excess is added and time allowed to redissolve the hydroxide first precipitated. This is true even when a very great excess of zinc is present, such as would obtain when 10, 20, 30, and 40% alloys of zinc with copper in 1 gram quantities were dissolved in 100 cc. and the copper reduced in amount until it was $N/3000$. These are the practical conditions met with in the electrolytic separation of copper from zinc.

$N/35,000$ copper solutions containing the excess in amounts of zinc just mentioned gave very unsatisfactory results with ferrocyanide, however, because of the precipitation of zinc ferrocyanide. This reagent was, therefore, useless in the presence of zinc.

Conclusions.—I. The contradictory state of the literature indicates that results in colorimetric examinations are not comparable unless the volumes worked with and the diameter of the apparatus used are at least approximately known.

II. It has been found with the method used that the end point of an electrolytic precipitation of copper, no other metals being present, may be detected by

Ammonium hydroxide	with an error not greater than 0.105%
Ammonium sulfide	with an error not greater than 0.015%
Potassium ferrocyanide	with an error not greater than 0.009%

provided the volume of the electrolyte was 100 cc. and there was originally present one gram of copper.

III. The recommended procedure for the detection of traces of copper at the end of electrolytic copper precipitation in the kinds of solutions indicated, is as follows: Take one cc. of the sample in a narrow test tube constructed as described. Make alkaline with ammonium hydroxide, acidify with glacial acetic acid, and add two drops of 2% $K_4Fe(CN)_6$ solution. A pronounced red color indicates more than 1 mg. of copper. Make similar additions to another tube as a blank, replacing the sample to be tested by distilled water. If by comparison the tubes are practically of the same color, then there is present not more than 0.1 mg. of copper in 100 cc. of the solution.

LABORATORY OF INDUSTRIAL CHEMISTRY.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CLARK UNIVERSITY.]

OUTLINE OF A THEORY OF HOMOGENEOUS CATALYSIS.[1]

BY M. A. ROSANOFF.

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The word catalysis was introduced about eighty years ago by Berzelius. It grouped together phenomena that had up to that time remained unconnected. But while a great and increasing number of new catalytic phenomena were discovered in subsequent years, the concept itself remained vague until Ostwald introduced his well known definition based on the conception of velocity of chemical change—a conception which was born with modern chemical kinetics and was unknown to Berzelius. According to Ostwald, a catalyzer is a substance whose presence *hastens* a given chemical reaction, although the reaction would also take place in its absence. Ostwald believes that a catalyzer exists for every reaction and, conversely, that any given substance is capable of catalyzing some reaction.

The object of the present communication is to tentatively propose some modifications of this conception of catalysis. The ideas formulated here will sound partly familiar, partly more or less new. What I have attempted to do is, to construct a theory involving few hypothetical assumptions, yet definit enough to be of practical service as a working-theory, or at least as a basis for further discussion. Only experimental research can really prove or disprove a theory of this type, and I should not take the liberty of publishing the present outline if its ideas were not

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[1] Presented before the New York Section of the American Chemical Society, October 11, 1912.