ble in the usual way. When all the soluble material had been removed, except the small amount in the upper rim, the crucible was filled about half full of water,

suction was applied and a moistened rubber stopper was quickly pressed down on top of the crucible. (The rubber stopper was always polished to a plane surface and washed free from any dust before using the first time.) As soon as the stopper was firmly held by the suction, water was poured on top of the holder (see figure) and around the stopper. The water drawn through the top rim easily completed the washing, as was indicated by the fact that no test for alkalinity could be obtained by addition of a drop of phenolphthalein to the edge of the crucible.

Continuous use of the crucible holder, since it was not designed for treatment in this manner, tended to crack the flange from the outer portion of the holder. A slight modification of the flange construction would perhaps lessen this difficulty.

RAPID DETERMINATION OF SMALL AMOUNTS OF COPPER BY THE IODIDE METHOD

By H. F. Bradley

PARK CITY, UTAH

Received April 5, 1920

The precipitate of cupric sulfide (containing not over 0.05 g. copper) is washed free from chlorides (complete removal of iron not being necessary), then moistened with a few drops of strong neutral zinc nitrate solution (free from chlorides), and ignited.

The residue of zinc oxide and cupric oxide is quickly dissolved by warming with 1 cc. of 1 : 2 hydrochloric acid. Neutralize with 5 per cent potassium hydroxide, acidify with acetic acid, add a little phosphate solution to prevent the action of iron,¹ then add 2.5 g. solid sodium iodide and titrate as usual.

SOME AMERICAN-MADE CHEMICAL REAGENTS

By W. D. Collins

BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

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I—POTASSIUM FERRICYANIDE

A member of the AMERICAN CHEMICAL SOCIETY informed the Committee on Guaranteed Reagents that he had found potassium ferricyanide purchased a year or two ago wholly unsuited for use in making the gelatin test on tin plate. The salt made a turbid green solution.

Examination of two lots which had been in the Bureau of Chemistry for several years showed that

¹ R. H. Deakin, *Chem. News*, 118, 193.

they were of the same quality, but a single recrystallization from a filtered solution gave a perfectly satisfactory product.

Correspondence with manufacturers and dealers secured some analytical reports which indicated material of high purity. A sample furnished as representing the product now sold by one manufacturer made a perfectly clear 10 per cent solution with no traces of green color and no precipitate.

It therefore appears that no one need now accept potassium ferricyanide which will not make a 10 per cent solution without any precipitate or green color. Purification of poor material in stock is worth while in most cases.

II—METHYL ORANGE¹

Similar complaint was made to the Committee of difficulty in procuring satisfactory methyl orange from American manufacturers. At the suggestion of the Committee, samples were purchased from four different sources. There was at hand for comparison one of a well-known foreign make. A sixth sample was obtained from a lot of methyl orange which was exhibited by a manufacturer at a meeting.

A few grams of the best appearing sample (Sample A) were repurified by precipitating the free acid, filtering, dissolving with sodium carbonate solution, and recrystallizing twice. This produced shining crystal leaflets of a beautiful orange-red color which were provisionally adopted as a standard.

The samples were judged by general appearance, odor, water-insoluble residue from one gram in 400 cc. of water, and indicator value. The results are given in the accompanying table.

COMPARISON OF SAMPLES OF METHYL ORANGE

SAMPLE	Appearance	Odor	Water-insol. Residue from 1 g.	Indicator Value	Notes
Standard	Orange-red crystals	None	0.0000	Good	
A	Orange-red crystals	Very faint	0.0008	Good	
B	Yellow-red powder	None	0.0294	Good	Foreign-made
C	Yellow-brown, lumpy ¹	Decided	0.0105	Good	
D	Brown, lumpy	Decided	0.0537	Fair	Dyestuff
E	Brown powder	Strong	0.1167	Good	Naphthol-like odor
F	Yellow-red powder	None	Slight	Good	

¹ A later sample from the manufacturer of C compared favorably with B or F.

The odor resembled aniline in three cases, and one sample smelled strongly like naphthol.

The two brown samples were not very pleasing in appearance. The manufacturer of one of these products stated in reply to criticism of his output that it was not intended for an indicator but was sold for use as a dyestuff.

A portion of Sample D was purified both by direct recrystallization and by precipitating the acid and subsequently neutralizing the free acid with soda. In each case a bronze-yellow crystalline powder was recovered which, in appearance, did not resemble the standard methyl orange. When used as an indicator its alkaline solution was bright yellow in color, but the acid solution was only pale red. Sample D did not give a clear solution when filtered.

Notwithstanding the poor quality of some of the samples obtained, the results show that it is entirely

¹ In collaboration with G. C. Spencer.

possible at this time to secure a very satisfactory grade of methyl orange. It is recommended that purchasers specify methyl orange of a grade to be used as an indicator and also stipulate that the insoluble residue from one gram dissolved in 400 cc. of water shall not exceed 0.025 g.

III—SULFURIC ACID FREE FROM NITRATE: THE DIPHENYLAMINE TEST FOR NITRATES¹

The diphenylamine test for nitrate has been studied carefully by J. Tillmans,² who reviews previous work and describes the best conditions for making the test. The most satisfactory reagent is prepared by dissolving 0.017 g. of diphenylamine in 100 cc. of concentrated sulfuric acid (sp. gr. 1.84), and adding 30 cc. of water.

At a time when there was no sulfuric acid in the Bureau of Chemistry which would give a colorless reagent, four producers and dealers were asked whether they could furnish such acid. Dealer A stated that they had never handled acid which would give absolutely no color under the conditions described, but that one grade furnished by Maker C was the nearest this quality which they had received. Producer B stated that they could not furnish acid which would not give a trace of green color, but at a later date stated that they were then able to furnish the required acid on request. Producer C stated that they could furnish such acid if reference was made to their letter on the subject. This acid proved perfectly satisfactory for making the reagent. Producer D stated that all their acid was of the quality desired. One bottle was ordered for examination. The blue color developed on making the reagent was darker than was obtained with any of the samples of acid on hand in the Bureau, and the acid was returned to the dealer.

This experience shows that sulfuric acid can be secured which will serve for preparing the diphenylamine reagent, but this grade must be specified clearly, and purchased subject to examination.

The very low limits for sensitiveness reached by Tillmans were not found in the tests for nitrates in sulfuric acid. He and others have pointed out the number of other substances which produce the blue color. It must be understood that a positive test does not prove the presence of nitrates, but a negative

result shows the absence of the minimum quantity necessary to give a test.

METHOD OF NITRATE TEST

A number of methods of applying the diphenylamine test were tried in order to select one which would serve to assure sulfuric acid sufficiently free from nitrates for careful analytical work without making the test too exacting. The U. S. Pharmacopeia test prescribes mixing the acid with nine volumes of water and pouring the mixture carefully over a reagent made with 0.5 g. of diphenylamine dissolved in 100 cc. of sulfuric acid and 20 cc. of water. Sulfuric acid containing 0.02 per cent N_2O_5 gives a blue ring at the place of contact of the two layers. Acid with 0.01 per cent N_2O_5 gives no color.

A simple application of the test is to add a drop or two of the U. S. Pharmacopeia reagent to 3 to 5 cc. of the acid in a test tube and overlay with water. A blue ring develops in 10 min. if the acid contains 0.00002 per cent of N_2O_5 . With 0.00001 per cent the ring is seen in some instances and not in others.

When 2 cc. of sulfuric acid are mixed with 1 cc. of water and there are added immediately to the mixture 1 cc. of reagent made with 0.017 g. diphenylamine, 100 cc. of sulfuric acid (sp. gr. 1.84), and 30 cc. of water, a decided blue color develops in 10 min. if the acid contains 0.00005 per cent N_2O_5 . If the mixture of acid and water is cooled to 20° C. before addition of the reagent, no blue color is developed in 10 min. if the acid contains less than 0.0001 per cent N_2O_5 . Nearly all the reagent sulfuric acid on the market will pass this test.

The presence of too large a quantity of diphenylamine interferes with the test. Increasing the proportion of either water or sulfuric acid in the reagent as described by Tillmans makes the test less sensitive. The preparation of the reagent is thus the most delicate test for the presence of nitrates, nitrites, or some of the other substances which give the blue color with diphenylamine. Sulfuric acid containing 0.000008 per cent N_2O_5 shows a decided faint blue color in 2 hrs. after preparing the reagent. Acid with less nitric present will serve to prepare a reagent which will be perfectly colorless.

Acid of this grade can be purchased if it is specified that this test must be met.

ADDRESSES AND CONTRIBUTED ARTICLES

CERTAIN ASPECTS OF THE CHEMISTRY OF CELLULOSE ACETATE FROM THE COLLOIDAL VIEWPOINT¹

By Gustavus J. Esselen, Jr.

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If one were asked for a good example of a colloidal solution in a non-aqueous solvent, probably among the first materials to come to mind would be solutions of cellulose esters. In spite of this, it is only comparatively recently that the colloidal character of the parent substance cellulose has been recognized.

¹ Read at the 59th Meeting of the American Chemical Society, St. Louis, Mo., April 12 to 16, 1920.

Harrison¹ has correlated in a most interesting manner many of the reactions of cellulose, as, for example, its behavior when treated with alkalies, acids or oxidizing agents, by considering the typical cellulose, cotton, as existing in a number of different degrees of colloidal dispersion. Cross² has also referred to cellulose as a colloid, and Miss Minor³ has recently considered the hydration of cellulose in paper making from the standpoint of colloid chemistry. Whether or not the solution of the prob-

¹ *Trans. Nat. Assoc. Cotton Mfrs.*, **101** (1916), 201. 2nd Report on Colloid Chem., Brit. Assn. Adv. Sci., **1918**, 52.

² *J. Soc. Dyers Colourists*, **34** (1918), 92.

³ *Paper*, **25** (1919), 700.