sidered negligible. The final volume was arbitrarily selected, as it was the greatest volume at which 0.1 cc. of 0.2 per cent dextrose solution would make a distinct change in color.

A test tube of the size given prevents much exposure to the air, and its liability to boil over when heated too rapidly, prevents excessive evaporation.

Numerous trials were at first made with ferrous sulfocyanide[1] and iodide starch mixture,[2] but it was found that both have a common defect; namely, they become colored on exposure to air without addition of Fehling solution. Attempts to obviate this destroy their sensibility to a large extent. The writer had used sodium monosulfide for some time for colorimetric copper estimations and was impressed by its sensitiveness. Furthermore, there ought to be no tendency for the reoxidation of the copper on mixing with the indicator, as the medium is a reducing one. After a few minutes a yellow color will appear, owing probably to solution of some of the copper sulfide. The absence of color, however, is permanent for sufficient time for an observation to be made, while when copper is unreduced, the appearance of the color is immediate. After the operator has become familiar with the end point, it can be judged very closely by the appearance immediately on addition of the drop. As long as unreduced copper is present, a yellowish color is perceptible without agitation, while when all the copper is reduced, the only shade is the reddish brown of the cuprous oxide.

Proteins, and metals which give colored sulfides interfere with the end point. For the former, the writer boils a measured volume and adds alumina cream while still hot, then cools and makes up to a convenient volume, adding sufficient water to correct for the volume occupied by the alumina. The solution can then be allowed to settle and the clear supernatant liquid used, or if time is an object, it may be filtered. This method works very well on most urines and colored solutions. For removing the metals, methods will doubtless suggest themselves.

RESULTS OBTAINED

Various dilutions of a sugar solution were made up and given to a member of the staff (without information as to their sugar content), who obtained the following figures.

No. of cc. used in titration	Mg. total dextrose present
23.30	47.60
15.65	47.75
11.70	47.60
9.35	47.75

It must be understood that this was not pure dextrose, as the purpose was only to see whether results were constant and independent of the concentration of the titrating solution over comparatively wide limits. The above results were each obtained with one titration besides the preliminary one.

Impure maltose solutions were titrated in a similar manner.

No. of cc. used in titration	Mg. total maltose present
23.2	92.8
15.5	93.0
11.6	92.4
9.25	92.5

The following results show the remarkable constancy of results over long periods. The titrations are on 5 cc. of mixed Fehling solution, which was the original manner of using the method, but it was changed to increase the accuracy of the end point.

6/11/1914 5 cc. Fehling reduced by 44.43 mg. crude maltose
8/26/1914 5 cc. Fehling reduced by 44.47 mg. crude maltose

For each value four concentrations were titrated. This constancy is not confined to maltose, but is also true of dextrose. The dextrose factor for 5 cc. in May was 23.6 mg. and in August 23.8 mg.

The writer advises the standardization of the Fehling solution by each user, and hence his factor should not be accepted as final. A mean of four determinations on pure glucose from two different sources in which the maximum variation from the average was ±0.15 mg., gave 47.5 mg. dextrose as the value of 10 cc. of a Fehling solution whose copper content had been accurately adjusted by a sodium thiosulfate solution standardized with pure copper. As can be seen, the factors, once obtained, need be determined only at rare intervals. Pure dextrose, prepared by the Bureau of Standards, is now available for this purpose.

SUMMARY

The writer describes a modification of Fehling's volumetric method designed to do away with some of its sources of error.

The use of a new indicator is described which, so far as is known, is here first used for that purpose.

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[1] Ling Rendle and Jones, Allen's "Commercial Organic Analysis," 4th edition.

[2] F. F. Harrison, Sutton's "Volumetric Analysis," 10th edition.

A COMPARISON OF THE GUNNING-COPPER METHOD WITH THE KJELDAHL-GUNNING-ARNOLD METHOD FOR THE DETERMINATION OF NITROGEN

By OVE F. JENSEN

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In 1908 the Association of Official Agricultural Chemists officially adopted[1] a modification of the Gunning method for the determination of nitrogen which prescribes the use of 0.1 to 0.3 g. of crystallized copper sulfate in addition to the potassium sulfate. Penny,[2] in his report on the determination of nitrogen in 1907, says of this modification: "The claims made for the catalytic action of copper sulfate seem to be justified by experience, and there is reason to suppose that this reagent will do much to shorten the time of digestion." Although possessing many advantages over the other methods in use at that time, it was not generally adopted. More recently another modification known as the Kjeldahl-Gunning-Arnold[3] method has been proposed. This method differs from the Gunning-Copper method, only in the use of metallic mercury instead of copper sulfate. In a recent number of THIS JOURNAL,[4] Trescot shows, very conclusively,

[1] U. S. Dept. Agr., Bureau of Chemistry, *Bull.* **122**, p. 183.

[2] *Ibid.*, **116**, p. 43.

[3] *Ibid.*, **108**, p. 15.

[4] Vol. **5** (1913), 914.

that the Kjeldahl-Gunning-Arnold method reduces the time of digestion over the original Kjeldahl or Gunning methods from four hours to one and one-half hours. This is a very important item in laboratories where a large number of nitrogen determinations are being made. The Gunning-Copper method has been in use in this laboratory for the past nine years, and the general practice has been to digest from two to three hours after the solution becomes clear.

Since this method possesses several advantages in manipulation over the Kjeldahl-Gunning-Arnold method, a comparison of the two methods with different periods of digestion was undertaken, using bone meal, dried blood, cyanamide, and linseed meal as representative substances. In Table I, the period of digestion in all cases refers to the length of time after the solutions became clear. In the length of time required to become clear, no difference was noted in the two methods. Using a moderate flame, the time required for the sulfuric acid solution to become clear was as follows:

Bone meal	25 min.	Cyanamide	20 min.
Dried blood	25 min.	Linseed meal	35 min.

TABLE I—EFFECT OF DIFFERENT PERIODS OF DIGESTION ON PERCENTAGES OF NITROGEN FOUND

Period of digestion after solutions became clear	1 hour				1½ hours				2 hours				3 hours			
METHOD	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.	No. of analyses	Max.	Min.	Av.
BONE MEAL:																
Gunning-Copper	6	2.18	2.16	2.16	4	2.20	2.18	2.19	6	2.20	2.18	2.19	6	2.23	2.20	2.20
Kjeldahl-Gunning-Arnold	6	2.25	2.19	2.20	4	2.20	2.18	2.19	6	2.23	2.19	2.20	6	2.22	2.20	2.20
DRIED BLOOD:																
Gunning-Copper	6	14.11	14.03	14.07	6	14.24	14.07	14.13	6	14.32	14.15	14.22	6	14.40	14.23	14.29
Kjeldahl-Gunning-Arnold	6	14.32	14.11	14.24	6	14.32	14.19	14.29	6	14.30	14.19	14.25	6	14.34	14.15	14.26
CYANAMIDE:																
Gunning-Copper	6	15.75	15.37	15.52	6	15.62	15.50	15.53	6	15.67	15.46	15.55	6	15.58	15.50	15.53
Kjeldahl-Gunning-Arnold	6	15.62	15.46	15.55	6	15.54	15.41	15.49	5	15.62	15.50	15.55	6	15.62	15.50	15.55
LINSEED MEAL:																
Gunning-Copper	6	5.53	5.45	5.49	5	5.62	5.50	5.57	6	5.62	5.50	5.55	6	5.64	5.56	5.62
Kjeldahl-Gunning-Arnold	6	5.62	5.53	5.56	4	5.62	5.59	5.61	6	5.59	5.53	5.58	6	5.62	5.56	5.58

The results seem to indicate that a digestion of one and one-half hours is sufficient to produce a quantitative yield of ammonia in either method, except in the dried blood, where from two to three hours are necessary in the Gunning-Copper method. Hibbard[1] found three hours to be necessary, using this method. On the whole, the results are slightly in favor of the Kjeldahl-Gunning-Arnold method, as a quantitative yield of ammonia is produced after a digestion of from one to one and one-half hours. However, it is doubtful if there are many substances for which the Gunning-Copper method will not give an equally high yield with the same length of digestion. In order to test this point, determinations were made on a number of substances such as are encountered in a fertilizer or food laboratory. Three determinations were made on each substance by each method. The data are given in Table II.

TABLE II—DETERMINATIONS OF NITROGEN ON VARIOUS SUBSTANCES

METHOD	Gunning-Copper			Kjeldahl-Gunning-Arnold		
Period of digestion	1½ hours			1½ hours		
SUBSTANCE	Max.	Min.	Av.	Max.	Min.	Av.
Gelatin	15.14	15.12	15.13	15.16	15.04	15.09
Egg albumin (dried)	12.86	12.75	12.80	12.86	12.80	12.83
Peptone	14.49	14.38	14.45	14.49	14.38	14.43
Casein	13.87	13.81	13.83	13.92	13.81	13.85
Feathers	14.49	14.43	14.47	14.54	14.38	14.46
Leather	4.83	4.72	4.76	4.80	4.75	4.78
Fish scrap	6.48	6.35	6.43	6.51	6.43	6.47
Animal tankage	6.32	6.26	6.31	6.35	6.29	6.33
Garbage tankage	2.99	2.96	2.98	3.00	2.96	2.99
Beef scraps	9.14	8.97	9.04	9.05	8.97	8.99
Castor bean pomace	4.66	4.55	4.59	4.55	4.52	4.53
Cocoa	4.01	3.94	3.97	3.97	3.90	3.93
Cottonseed meal	7.33	7.30	7.31	7.29	7.24	7.26
Cottonseed meal	6.43	6.40	6.42	6.37	6.32	6.35
Silage (dried)	1.30	1.26	1.28	1.29	1.26	1.27
Flour	2.43	2.41	2.42	2.44	2.43	2.43
Bran	2.60	2.55	2.58	2.58	2.58	2.58
Bone meal	3.06	3.02	3.04	3.11	3.02	3.07
Peat	2.41	2.37	2.38	2.37	2.36	2.37

The results obtained for these substances by the two methods show a very close agreement, and in point of accuracy there is no choice between them. The Gunning-Copper method possesses several distinct advantages over the other which may be enumerated as follows:

I—The use of potassium sulfide is unnecessary, and thus one detail of manipulation (addition of K_2S) is eliminated, slightly shortening the time required for the determination. Also the presence of hydrogen sulfide in the laboratory from this source is avoided.

II—In adding the sodium hydroxide before distilling, the copper sulfate acts as an indicator, so that a large excess of alkali is easily avoided, and the bumping during distillation is much lessened.

III—The difference between the price of copper sulfate and metallic mercury, and the elimination of potassium sulfide, makes the Gunning-copper method somewhat cheaper.

SUMMARY

A quantitative yield of ammonia in dried blood is produced sooner in the Kjeldahl-Gunning-Arnold method than in the Gunning-Copper method. In the case of all the other substances studied, a digestion of one and one-half hours proved equally efficacious for either method.

The Gunning-Copper method possesses advantages in manipulation which make it preferable to the Kjeldahl-Gunning-Arnold method, especially where a large number of determinations are to be made.

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[1] THIS JOURNAL, **2**, 464.

COMPARISON OF A FEW METHODS FOR TOTAL PHOSPHORIC ACID IN SUPERPHOSPHATE[1]

By C. A. PETERS

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A comparison of several methods for the determination of total phosphoric acid in superphosphate has been made, emphasizing the interference of silica in the gravimetric method, and showing that shorter methods give as accurate results as the customary double precipitation as phosphomolybdate and ammonium

[1] Taken from a thesis by Arthur G. Weigel, optionally presented for the degree of B.S. at the Massachusetts Agricultural College at Amherst.