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Jack J. Hinman Jr.
State University of Iowa

W. Keith Weeber
Illinois State Department of Health

R. Rupert Kountz
State University of Iowa

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AMMONIA AND ORGANIC NITROGEN DETERMINATIONS IN STREAM POLLUTION STUDIES

JACK J. HINMAN, JR., W. KEITH WEEBER¹ AND
R. RUPERT KOUNTZ

Determinations of ammonia in water supplies go back to the time of Chevreul in 1811. Titration procedures for the estimation of the substance were worked out by Boussingault (2), Bineau (1) and Thompson (9) during the 1850's. And there are already numerous modifications of the method for the estimation of total organic nitrogen developed by Johann Kjeldahl (6) in the Carlsberg Laboratory, in Copenhagen, in 1883.

It is not meant to imply, by the title given this paper, that basically new and original methods for the determination of nitrogen as ammonia or in its organic compounds are to be presented. Only modifications of the procedures and of the apparatus commonly employed in these determinations will be described. However these modifications have been found helpful in our laboratory work on specimens of sewage and of stream waters and it is believed that other persons who are required to analyze large numbers of such samples may also find the modifications advantageous.

Briefly, the procedure followed involves the preliminary removal of the ammonia by distillation of the sample and the collection of the evolved ammonia in a definite volume of a standard acid solution, with subsequent titration of the excess acid remaining, using methyl red indicator. The residue in the distillation flask is then digested with mixed phosphoric and sulfuric acids in the presence of a copper selenate catalyst with the object of converting the nitrogen of the organic compounds into ammonium sulfate and its estimation in the same manner as was adopted for ammonia nitrogen originally present. In the digestion a convenient and somewhat novel all-glass apparatus is employed.

The copper selenate catalyst, recommended by Campbell and Hanna (3) in 1937, has been found helpful in accelerating the digestion and thus speeding up the work. The modification of the manner of preparing the catalyst solution worked out by Mr. Clyde M. Berry, Research Assistant in Pediatrics, at the University of Iowa, has simplified and facilitated the preparation of the reagent.

¹ Now District Engineer, Illinois State Department of Health.

Titration of the ammonia distilled from the specimen as received, and after digestion of the nitrogen compounds, has been preferred on account of the fact that larger portions of polluted waters may be used and that less multiplication of experimental errors is necessary in estimating the number of milligrams of nitrogen in a liter of the liquid. Portions of 250 milliliters of sewage, or even more, may be taken for the work. Such portions are usually more representative than smaller ones on account of the large amount of non-homogeneous suspended matters which are to be expected in sewage. When large quantities of nitrogen are present in the distillate, the Nessler color comparison process is difficult unless very small aliquot portions are taken for the test. Consequently the value obtained, with its included error, must be multiplied by a large number. Other difficulties can be avoided if a titration process is substituted for the Nessler procedure. Among these difficulties are the interference of turbidities produced in the color standards by minute amounts of alkaline earth salts sprayed over in distillation, the color intensity differences due to difference in temperature of the color standards and the unknowns, and the color abnormalities, tending toward the lemon yellows, produced by the reaction between the Nessler reagent and various amines.

The ease of employment and economy of installation of the all-glass apparatus used in the digestion process will be separately described. In a crowded laboratory, where fume ducts and fume stacks would be expensive to install, this apparatus filled a real need and expedited the routine analysis of stream waters and sewage samples to a surprising degree.

PART I

THE PROCEDURE

The Reagents.

1. N/100 Sulfuric Acid Solution.

This solution is prepared by diluting special nitrogen-free sulfuric acid (analytical grade) with ammonia free distilled water. It is standardized and adjusted in strength until correct, as found by titrating against anhydrous sodium carbonate of analytical grade, which has been oven-dried at 103°C. and preserved in a desiccator until taken for the titration. The adjustment of the N/100 sulfuric acid solution to correct strength within the limits of experimental error, is a material time saver in comparison with the use of a normality factor. The solution is usually prepared in ten liter quantities and stored in a pyrex glass carboy.

1 milliliter N/100 Sulfuric Acid = 0.00049 gm. H_2SO_4

1 milliliter N/100 Sulfuric Acid = 0.00014 gm. N as NH_3

2. N/100 Sodium Carbonate Solution.

This solution is prepared by dissolving the required amount of oven-dried sodium carbonate (analytical grade) in ammonia-free water. The amount of the material to be weighed out is 0.5300 grams per liter of solution to be prepared. If necessary, the solution is adjusted so that one milliliter of it is exactly equivalent to one milliliter of N/100 sulfuric acid solution, Reagent No. 1, when methyl red is used as the indicator. The N/100 sodium carbonate solution is also stored in a carboy of pyrex glass.

3. Ammonia-Free Distilled Water.

Distilled Water is passed through a column of Folin's Permutit to remove the ammonia it contains. The effectiveness of the ammonia removal is checked by the use of the Nessler reagent.

4. Copper Selenate Catalyst Solution.

Powdered black elementary selenium is oxidized by the aid of nitric acid and heat. About 25 grams of the substance is placed in a one-liter flask *under a hood* and dilute nitric acid (1:1) is slowly added until action ceases. Heat is then cautiously applied. It is important to use a large flask because the mixture foams vigorously. The poisonous nature of selenium and of selenium fumes should be kept in mind.

Excess oxides of nitrogen must be removed from the material by evaporating the mixture to dryness, dissolving in water and repeating the evaporation to dryness at least three times. The residue must be white. Any yellow color indicates failure to remove all of the nitrogen oxides resulting from oxidation of the selenium. This calls for another dissolving of the residue and another evaporation to dryness.

One gram of the dried selenium oxide, prepared as above, and one gram of copper sulfate of analytical grade, are to be dissolved in 100 milliliters of a mixture of one part syrupy phosphoric acid and three parts of concentrated sulfuric acid, nitrogen free. Mr. Berry's procedure, which expedites the preparation of the reagent, consists of dissolving the selenium oxide and the copper sulfate separately in the minimum quantity of ammonia-free distilled water and then adding, first, the selenium solution, and second, the copper solution to the required quantity of phosphoric acid, (25 milliliters for each 100 milliliters to be prepared). Finally the concentrated sulfuric acid is added to bring the solution to the predetermined volume.

The resulting copper selenate catalyst solution is very poisonous as well as very corrosive.

5. Sodium Hydroxide Solution, approximately 7.5N.

Dissolve 300 grams of sodium hydroxide (nitrogen free) in sufficient ammonia-free distilled water to make a liter of solution.

6. Methyl Red Indicator Solution.

Dissolve 2.0 grams of powdered methyl red (indicator quality) in 1000 mls. of 60% ethyl alcohol.

7. Phenolphthalein Indicator Solution.

Dissolve 5 grams of phenolphthalein (indicator quality) in 1 liter of 50% ethyl alcohol.

Ammonia Determination.

Place 250 mls. of the sample of water or sewage in an 800 ml. Kjeldahl flask made of heavy pyrex or resistance glass. If the strength of the sewage is very great, it may be desirable to use only 100 mls. of the sample and dilute to 250 mls. with ammonia-free distilled water.

A phosphate buffer solution, such as is recommended in Standard Methods of Water and Sewage Analysis, APHA and AWWA, 8th edition, 1936, based on the work of Nichols and Foote (4-7), may be used. Experience with many Iowa stream waters and wastes has indicated that the carbonate and bicarbonate content of Iowa waters provides sufficient buffering in most instances. The avoidance of the buffer solution, if not needed, reduces the amount of sulfuric acid required for neutralization of the water when the digestion stage of the procedure is reached in the determination of organic nitrogen.

The Kjeldahl flask is connected to a condenser, heat is applied and distillation is commenced. The outlet tube of the condenser is adjusted to reach almost to the liquid surface of 25 mls. of N/100 sulfuric acid solution which have been exactly measured into a pyrex erlenmeyer flask of about 500 mls. capacity. To the acid solution is added exactly 0.5 mls. of the methyl red indicator solution. The distillation is continued until 200 mls. of the liquid in the Kjeldahl flask have distilled over. It is advantageous to conduct the distillation rather slowly at first, when the ammonia will be most rapidly evolved. Toward the end of the distillation the rate of boiling may be increased and the receiving flask may be lowered somewhat, as there will be less ammonia in the steam being condensed. The point at which 200 mls. of the sample have been driven over may be conveniently indicated with sufficient exactness by marking on the receiving flask with a glass-marking pencil. (Fig. 1.)

A "blank" of 250 mls. of ammonia-free water is distilled at the same time and in the same manner as the unknown samples being examined,

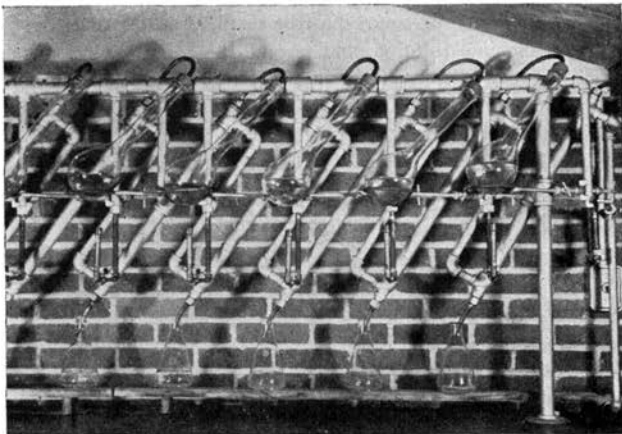


Fig. 1

in order to check the purity of the reagents and to be used in establishing the titration endpoint.

The titration is conducted as follows: To the distillate from the blank are added exactly 25 mls. of the standard N/100 sodium carbonate solution and the mixture is stirred. The methyl red contained in the mixture tints the liquid and establishes the color to which the unknowns are to be titrated. The distillates from the unknowns are then titrated by adding N/100 sulfuric acid solution to them from a burette until the color produced exactly matches the color of the blank. The amount of the N/100 sulfuric acid solution required to reach the endpoint corresponds to the quantity which was neutralized by the ammonia in the distillate. Since 1 milliliter of N/100 sulfuric acid solution, or of the N/100 sodium carbonate solution, is equivalent to 0.00014 grams, or 0.14 milligrams of nitrogen, in the form of ammonia, the calculation of the ammonia evolved is conducted thus:

$$\frac{1000}{\text{mls. of sample}} \times (0.14) \times (\text{mls. of N/100 acid}) = \text{ppm. N as NH}_3.$$

Determination of Organic Nitrogen.

As a rule no correction for the nitrates contained in the stream water or the sewage will be required. Except in freshly treated sewage there will probably be little or no nitrate nitrogen. If the amount of nitrate nitrogen exceeds five parts per million, and in some cases less, it may be necessary or desirable to introduce Scovell's (8) salicylic acid method for the inclusion of nitrates or Förster's (9) modification of it.

In the absence of the need for including the nitrates, or after the reduction of the aminosalicic acid by zinc or sodium thiosulfate, the analyst may proceed to the determination of the organic nitrogen content at once. To the residue in the distillation flask, add 10 mls. of the copper selenate catalyst solution. Place the flask on a digestion rack, apply heat and digest until the excess water has been driven off, all carbonaceous matter has disappeared and a pale green color remains in the clear

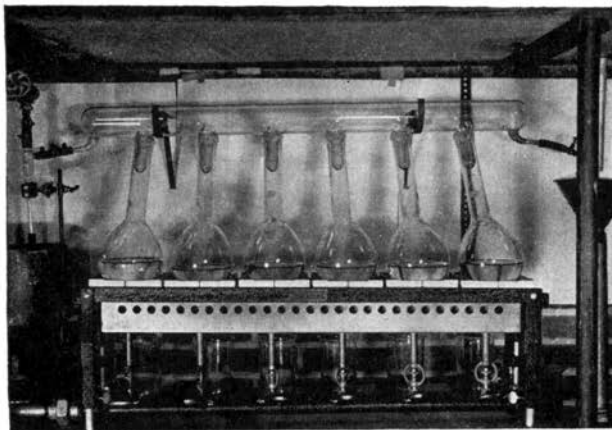


Fig. 2

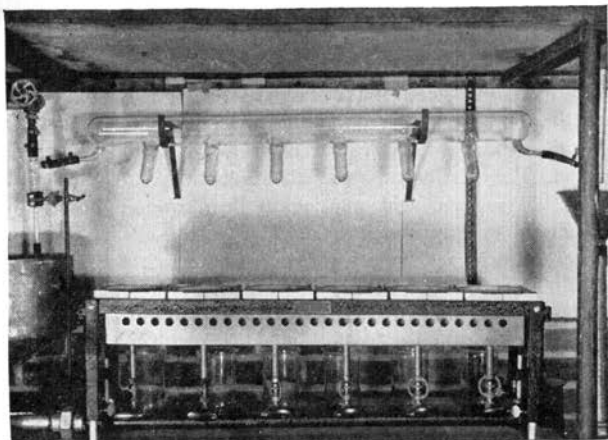


Fig. 3

liquid. This takes only a few minutes. Continue the digestion slowly for about five minutes thereafter. (Figures 2, 3.)

When the flask and contents are sufficiently cool, add 200 mls. of ammonia-free water and four or five drops of phenolphthalein indicator solution. Add concentrated sodium hydroxide solution, 7.5N, until alkaline. Remember that a heavy excess of the alkali may bleach the color of the indicator solution after it has once been formed.

Connect the digestion flask to a condenser and carry out the distillation of the ammonia produced by the digestion of the organic nitrogen compounds. Use the same procedure indicated under the heading of ammonia determination, including the preparation of a new blank. Calculate the amount of nitrogen in the same manner, but call this Organic Nitrogen.

PART II

THE APPARATUS

Distillation Flasks.

Heavy Kjeldahl flasks of pyrex, or other resistant glass, are recommended because the catalyst seems to act on the glass in such a way as to dissolve it slowly and in time leave minute holes. Heavy flasks can be used longer than thinner ones.

The Digestion Apparatus.

The fume-removal device for the digestion apparatus which we have used in our recent work is of pyrex glass. The digestion rack heating units which were available were provided with spaces for six flasks each. Our fume duct equipment was therefore made in units to accommodate six flasks. We have two such units in use and one in reserve.

The fume duct units each consist essentially of a pyrex glass tube about 2 inches in diameter with six 1-inch tubes four inches long attached at right angles as side-arms. The distances between the side-arm tubes

represent the distances between the centers of the flask spaces of the heating units. At each end of the large tube is a smaller, down-curved tube which can serve either as a point of connection to the air pump line or as a drain through which to remove acid condensation liquids from the fume duct. The ends of the large tube are closed.

The six side-arm tubes each have a bulbous portion near their junction with the main duct and all are carefully closed to a rounded aperture uniformly $\frac{3}{8}$ inch in diameter. If less than six specimens are to be digested at one time, fume removal may be assisted by closing the openings of the idle side-arm tubes with small corks. The diameter of the side arm tubes is such as to permit about $\frac{1}{8}$ inch all-around clearance between the tubes and the necks of the flasks which are to be slipped over them. By slipping the flasks up to the bulbous portion of the tube, the annular space may be reduced as desired.

Air is drawn into the flasks during digestion by means of an all-glass, water-jet vacuum pump, such as is commonly used in filtration work in the analytical laboratory. The pump selected is one which handles a large volume of air, rather than one which is necessarily able to produce a high degree of vacuum. In operation the air enters at the mouth of the flask, passes down along the side-arm tube and is drawn into the aperture at the end of the side-arm tube, carrying steam and acid fumes with it. The fumes are mixed with water in the jet of the air pump and pass to the sewer. Due to the alkaline character of the tap water available in our laboratory, the liquid entering the sewer is not acidic. (Fig. 4.)

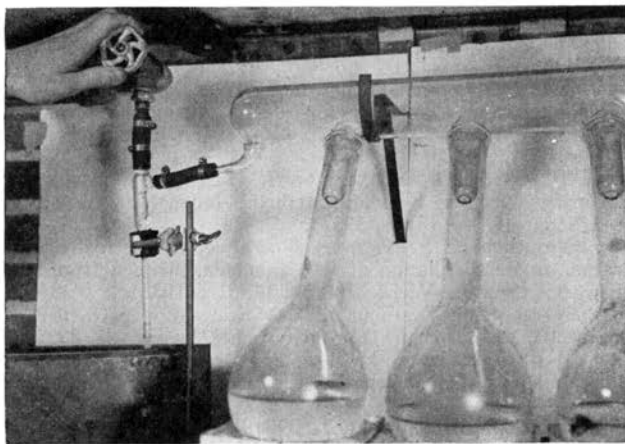


Fig. 4

The discharge from the air pump enters a funnel attached directly to a pipe leading to the sewer. The end of the pump discharge is kept above the rime of the funnel, so that if by any chance the funnel contained water and the pressure on the University's water supply system were to drop, there would be no possibility of "back-siphonage" of water from the funnel into the University drinking water supply. In this way neither sewage nor selenium contamination of the drinking water need be feared.

This preventive sanitary feature is used throughout the State Hygienic Laboratories wherever water from the university supply is discharged into the sewers.

Fumes from the digestions are confined to glass equipment except for the very small distance where rubber tubes, held by brass collars, connect the air pump and the fume duct. The fume duct itself hangs in a cradle of strap-iron so that it may be turned on its long axis. This permits freedom in placing and removing digestion flasks. The end of the fume duct nearest the air pump may be raised to cause all of the acid condensate collecting in the duct to drain to the opposite end of the duct, whence it may be drained away through a rubber tube normally kept closed by a pinch-cock or screw clamp.

This equipment for the removal of fumes has prevented the escape of fumes into the laboratory and the irritating or detrimental effects which would be produced thereby. No hood is used or needed. No odor of sulfur trioxide is perceptible, even when the fumes are rolling out of every flask attached to the duct. As long as water under pressure is available to the air pump, fans and vent pipes are unnecessary and acid fumes need not be discharged above the building where they might affect exterior finishes or damage metal roofing or gutters.

The fume ducts were made according to our plan by Mr. Herman Wiegand, glassblower of the Department of Chemistry of the University of Iowa.

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