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The Modifications of the Kjeldahl Method For the Quantitative Determination of Nitrogen.

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BY JOSEPH SAMUEL HEPBURN, A.B., B.S. in Chem., M.S. 108th Class,

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The element nitrogen is an absolute essential for organized matter, since it is a constituent of the proteins which occur in all forms of plant and animal life. Nitric acid and the nitrates play a prominent part in the arts, especially in the manufacture of fertilizers and in the preparation of nitro-glycerin, gun cotton and aromatic nitro compounds for high explosives. Nitrogenous compounds form the greater part of the large and growing family of coal tar dyes, among which may be mentioned those triumphs of synthesis, artificial indigo and alizarin. Synthetic

organic chemistry has given to medicine a host of remedies which contain nitrogen, such as antipyrine, antifebrin and phenacetin. Nitrogen is found in the alkaloids, in prussic acid—an exceedingly virulent poison; in ammonia—a powerful base; in various products of animal and vegetable origin, such as mustard oil and the derivatives of uric acid, and in a great series of synthetic compounds like the osazones which have been so helpful in the study of the structure of the sugars.

The quantitative determination of an element so widely distributed is of the utmost importance and has been the subject of careful study by many investigators. The methods of analysis fall into three classes, represented by Dumas, Will and Varrentrapp and Kjeldahl. The year 1908 marks the twenty-fifth anniversary of the publication of the original method of Kjeldahl.

The first method for the quantitative determination of the nitrogen content of an organic compound was the absolute method of Dumas. He heated the compound with cupric oxide in an atmosphere of carbon dioxide, reduced any oxides of nitrogen by means of a glowing spiral of metallic copper, passed the gases through a solution of potassium hydroxide and measured the volume of residual nitrogen.

Later on, Will and Varrentrapp devised a method for obtaining the nitrogen in the form of ammonia by heating the nitrogenous compound with soda-lime to redness; the ammonia was collected in hydrochloric acid and weighed as ammonium chloroplatinate. Peligot modified this process by using a known amount of standard acid, and then titrating the excess of acid. The methods of Dumas and Will and Varrentrapp required that the compound be in a fine state of division; solutions had to be evaporated to dryness and the residue finely divided.

Kjeldahl (1) worked on brewery materials and wished to determine the nitrogen content of various solutions without evaporating them to dryness. First he tried Wanklyn's method for determination of albuminoid nitrogen, which depends on distillation with alkaline permanganate; the yield of nitrogen was incomplete. Better results were obtained by boiling with potassium permanganate and dilute sulphuric acid, making alkaline with a fixed alkali, distilling into standard acid, and titrating the excess of acid. Finally the substance, whose nitrogen content was to be determined, was heated with concentrated sulphuric

acid and completely oxidized with permanganate. Kjeldahl says: "The principle of the new method, therefore, is to heat the substance in question for some time with a sufficient quantity of concentrated sulphuric acid to a temperature which is close to the boiling point of the acid, and then to oxidize the solution thus obtained with an excess of dry, powdered permanganate." He recommends heating with sulphuric acid, to which some fuming sulphuric acid and phosphoric anhydride have been added, for two hours. The dark solution is to be removed from the flame and the oxidation is to be completed by means of an excess of dry, finely divided potassium permanganate, which is added, a little at a time, in the form of a stream of dust. The dark solution becomes lighter, then colorless, finally dark green, or blue green if phosphoric anhydride be present. The solution may be heated gently, but not strongly, or nitrogen will escape. Kjeldahl diluted the solution, transferred to a distilling flask, made alkaline with a fixed alkali after adding zinc turnings to prevent bumping, distilled into a known volume of standard acid, added potassium iodide and iodate and titrated the liberated iodine with standard sodium thiosulphate. The per cent. of nitrogen was then calculated. Kjeldahl published excellent results on the determination by his method of the nitrogen content of twenty-three aliphatic and aromatic compounds, as well as naturally occurring bodies. Certain alkaloids, cyanogen and nitro compounds, gave poor results.

Heffter, Hollrung and Morgen (2) made two determinations of the nitrogen content of sixty-five substances by the method of Will and Varrentrapp, and duplicate determinations on the same substances by Kjeldahl's method. The means of the determinations by the two methods checked well, the average difference being 0.084%. The Kjeldahl method gave more nitrogen in 94% of all the determinations. They digested 1 to 1.5 grams of the substance with 2 grams of phosphoric oxide and 20cc. of a mixture of 4 volumes of pure concentrated sulphuric acid and 1 volume of the fuming acid. Heat was applied with a small flame until foaming ceased; then the solution was boiled, since this is essential for complete oxidation. The maximum period of digestion was five hours.

Petri and Th. Lehman (3) applied the process of Kjeldahl, including oxidation with potassium permanganate, to the de-

termination of the nitrogen content of ammonium sulphate, urea, uric acid, hippuric acid, kairin A (ethyl hydroxytetrahydroquinoline), and normal, diabetic and albuminous urines. They distilled the ammonia in a current of steam.

Pflüger and Bohland (4) digested urine with a mixture of equal parts of concentrated and fuming sulphuric acid, omitting the oxidation with permanganate. In a later paper (5) they recommend digestion of urine with fuming sulphuric acid.

Kreusler and Henzold (6) noticed that, during the distillation, the steam, which passed over with the ammonia, dissolved fixed alkali from the walls of the glass condenser, which neutralized the receiving acid and so caused a result which was too high. Kreusler (7) called attention to the fact that fuming sulphuric acid carries oxides of nitrogen, which reduce to ammonia during the digestion and thus increase the percentage of nitrogen. He used a solution of 200 grams of phosphoric oxide in 1 liter of rectified sulphuric acid.

Dafert (8) concluded that the sulphuric acid removes hydrogen and oxygen from the organic body in the proportions necessary to form water. The heating of the resulting carbonized mass with sulphuric acid evolves sulphur dioxide, which reduces the nitrogenous substance; the resistant nitrogen compounds thus formed are decomposed on the addition of potassium permanganate with the production of ammonium compounds. The quantity of ammonia formed depends essentially upon the length of the period of digestion; if this be sufficiently long, nearly all nitrogenous bodies will allow the complete conversion of their nitrogen content into ammonia. However, since the period of digestion, required by a new compound, cannot be foreseen in any way but must be ascertained in each case by special examination, the Kjeldahl method cannot replace entirely the method of Dumas. Dafert later (9) divided nitrogenous compounds into two classes. The first class may be examined by the Kjeldahl method without any previous reduction or other treatment; to it belong the amines, ammonium compounds, pyridine and quinoline derivatives, alkaloids and bitter principles, proteins and allied bodies. The second class includes all compounds which require a previous treatment, such as nitro, nitroso, azo, diazo, and amidoazo compounds, hydrazines and all the compounds of nitrous and nitric acids; in a word, all those compounds in the mole-

cules of which a nitrogen atom is linked to an oxygen atom or atoms, or to a second nitrogen atom.

Czeczetka (10) recommends that a saturated solution of potassium permanganate in pure, concentrated sulphuric acid be substituted for the solid salt in the final oxidation. The permanganate solution is run slowly into the solution to be oxidized by means of a tap-funnel with a long stem. Care must be taken that the permanganate solution flows into the digested solution without falling upon the surface of the latter; otherwise the reaction occurs with explosive violence.

Bosshard (11) applied the original method of Kjeldahl with excellent results in determining the nitrogen content of allantoin, and of a number of amino acids, including leucine, tyrosin, asparagin, aspartic, glutaminic and amido-valeric acids. He cautions against the use of sodium hydroxide containing nitrate in the distillation, since the nascent hydrogen, produced by the reaction between the zinc and sodium hydroxide, reduces the nitrate to ammonia and thus increases the percentage of nitrogen. Bosshard also noticed that, whenever a great excess of zinc and sodium hydroxide solution was used, sodium hydroxide was carried over mechanically by the hydrogen gas, and was titrated as ammonia. A ball filled with glass beads failed to hold back all of the mechanically carried alkali. However, the error may be overcome by avoiding a great excess of the reagents, or by the use of a safety distilling bulb such as that invented by Pfeiffer and F. Lehmann (12) and improved by Rindell and Hannin (13), or that devised by Reitmair and Stutzer (14).

Wilfarth (15) noticed that the presence of copper salts appreciably reduced the time required for the digestion; he tested the effect of the oxides of iron, mercury, manganese, bismuth, zinc, lead and copper on the digestion of materials such as clover hay and peas. One gram of material and one gram of oxide were digested with concentrated sulphuric acid and phosphoric anhydride until a bright Rhine wine color appeared. Digestion proceeded more rapidly when the oxides were added than when they were absent. Mercuric oxide reduced the time factor to one-eighth that of the plain digestion, but mercur-ammonium compounds formed in the distilling of the ammonia and caused a loss of nitrogen. Therefore, experiments were tried with cupric oxide.

The effect of the cupric oxide depends entirely on the quantity of oxide in solution; 20 cc. of concentrated or fuming sulphuric acid will dissolve 0.1 gram of oxide, but the same volume of acid will dissolve 0.2 gram of oxide in the presence of 4 grams of phosphoric anhydride, and 0.6 gram of oxide in the presence of 10 grams of anhydride. Wilfarth states that the cupric sulphate plays a catalytic rôle in the oxidation of the organic matter. For each digestion he used either 0.5 or 1 gram of monohydrated cupric sulphate and 20cc. of a solution of 250 grams of phosphoric anhydride in 1 liter of concentrated sulphuric acid. The mixture was heated until either colorless, or a wine red, when it was oxidized with permanganate. This method was applied with success to various materials of animal and vegetable origin, such as leather and oil cake.

In a second paper (16) Wilfarth states that the time factor is almost the same when ferric oxide is substituted for cupric oxide, but both the green color of copper and the yellow one of iron mask the end point of the digestion.

Mercuric oxide is more soluble in sulphuric acid, hence acts as a better catalyser, and it possesses the additional advantage of forming a colorless solution. Oxide, free from nitrate, prepared by the wet method, should be used; for it may be substituted a chemically equivalent quantity of metal or sulphate. One gram of substance should be digested with 0.7 gram of mercuric oxide and 20cc. of a mixture of 300cc. of concentrated and 200cc. of fuming sulphuric acid, without the addition of phosphoric anhydride, until completely colorless; 0.6 gram of the oxide dissolves while the other 0.1 gram prevents bumping during the digestion. While oxidation may be completed with permanganate after the solution becomes wine red, a loss of nitrogen may then occur. When mercuric oxide is substituted for cupric oxide, the time factor for a digestion is reduced to one half. The formation of mercur-ammonium derivatives during the distillation of the ammonia is prevented by an addition of potassium sulphide solution. The Official Agricultural Chemists, in their modification of this method (17), direct the use of 25cc. of a solution of 40 grams of sulphide in 1 liter of water.

Warington (18) and Reitnair (19) have devised methods whereby the organic nitrogen alone may be determined when a mixture of an organic compound and a nitrate is the subject of

analysis. Warington directs a preliminary heating of the mixture with an excess of ferrous sulphate and strong hydrochloric acid to expel the nitric nitrogen; the solution is then evaporated to dryness, concentrated sulphuric acid is added and the digestion is carried out in the usual way to determine the organic nitrogen. Reitmaier places one gram of the finely powdered mixture in a dish of tin foil, adds 3cc. of 50% sulphuric acid, stirs well with a glass rod, dries in the oven 3 to 4 hours at 60° to 80°C., then for one hour at 120°-130°C. The moist mass is now free from nitric acid, and is digested in the usual way.

Several investigators have modified the method of Kjeldahl so that it may be applied in the determination of the nitrogen content of nitrates and nitro compounds. Stebbins (20) digested 0.25 gram of material with 0.5 gram of sucrose, 2 grams of phosphoric anhydride and 20cc. of a mixture of four volumes of sulphuric acid of 66°B., and one volume of the fuming acid; oxidation was completed by means of permanganate. Results, correct to a few tenths of one per cent., were obtained with dinitrobenzol, meta nitraniline, and ortho nitrophenol.

Asboth (21) mixed 0.5 gram of such substances as azobenzol, nitrobenzol and picric acid with 1 gram of sucrose and digested with cupric sulphate and sulphuric acid, as directed by Wilfarth, without use of potassium permanganate. The same process was applied to cyanide, ferrocyanide and ferricyanide of potassium, sodium nitroprusside and ammonium thiocyanate, as well as to cyanuric acid. With nitrates, sucrose was replaced by benzoic acid; for each half gram of potassium nitrate, 1.7 grams of benzoic acid were added. Although permanganate was used to complete the oxidation, the results were low by 0.339 %. The Kjeldahl-Wilfarth process gave the best results with alkaloids. Quantitative results could not be obtained with pyridine, quinoline and cinchonine. Asboth used a solution of 350 grams of Rochelle Salt and 300 grams of sodium hydroxide in 1 liter of water in his distillations, in order to keep metallic oxides in solution.

Ulsch (22) introduced platinic chloride as a catalyser; his charge consisted of 1 gram of substance, 0.05 gram of cupric oxide, 5 drops of platinic chloride solution, which contained 0.04 gram of platinum in 1cc., and 20cc. of a solution of 200 grams of phosphoric anhydride in 1 liter of pure, concentrated sulphuric acid. This mode of digestion is more rapid than that with mer-

curic oxide; the digestion is finished when the solution takes on a pure green (not a yellow-green) color. Oxidation with permanganate is entirely omitted. Analyses are given of the nitrogen content of a number of substances of both animal and vegetable origin.

Jodlbauer (23) improved the process of Asboth for nitric nitrogen and combined with it the method of Ulsch. He replaced benzoic acid by phenol, which more readily yields nitro derivatives. Stannous chloride was first used to reduce nitrophenol to aminophenol, but did not act with sufficient energy, while zinc dust gave excellent results. Platinic chloride was used as the catalyser. From 0.2 to 0.5 gram of potassium nitrate, or the corresponding amount of another nitrate was digested for 4 hours with 20cc. of concentrated sulphuric acid, 2.5cc. of phenolsulphonic acid (50 grams of phenol dissolved in sufficient concentrated sulphuric acid to yield 100cc. of solution), 2 to 3 grams of zinc dust and 5 drops of platinic chloride solution of such strength that 1cc. contained 0.04 gram of metallic platinum. Addition of 4 grams of phosphoric anhydride to a charge reduced the period of digestion to two hours.

The Association of Official Agricultural Chemists have modified both the Kjeldahl and Gunning methods to include the nitrogen of nitrates. Salicylic acid is added to form a nitro compound, which is reduced by means of zinc dust or sodium thio-sulphate. The use of the latter reagent was first recommended by Förster (24).

Sherman (25) finds that a loss of nitric nitrogen always occurs whenever much chloride is present with the nitrate. A yield of 99.6% of the total nitric nitrogen is obtained by the official modified Kjeldahl method, if the solution of salicylic acid in sulphuric acid be cooled, added to the material and permitted to stand in contact with the same for two hours at room temperature, with frequent shaking. Zinc dust is then added, heat is applied, and the rest of the process is carried out as officially directed. The official modified Gunning method yielded but 97.8% of the total nitric nitrogen, although the acid mixture was cooled, the thiosulphate was added slowly and with cooling and shaking, and the digested material was boiled for some time after it became colorless.

Kulisch (26) determines the nitrogen content of wine,

must and yeast by digesting with metallic mercury and a mixture of equal volumes of concentrated and fuming sulphuric acid, which contains 100 grams of phosphoric anhydride in each liter. Must contains much sugar, which should be fermented by addition of so slight a quantity of yeast culture that the nitrogen content of the latter may be neglected; the fermented liquid is digested in the usual way.

The determination of the nitrogen content of coal has been studied by Schmitz (27) and Lord (28). Schmitz digests from 0.8 to 1.0 gram of coal with 1 gram of mercuric oxide and 20cc. of concentrated sulphuric acid for from 2 to 3 hours. He digests coke samples for 1 hour with 1 gram of mercuric oxide and 20cc. of concentrated sulphuric acid, then adds another gram of mercuric oxide in portions and 2 grams of finely powdered potassium permanganate in small portions. Lord digests 1 gram of coal with 30cc. of concentrated sulphuric acid and about 0.65 gram of metallic mercury. "The digestion was continued for about three-quarters of an hour after the oxidation was apparently complete, the total time being about three hours."

Arnold (29) studied the action of a mixture of sucrose, benzoic acid, cupric sulphate and mercury, with and without the addition of phosphoric anhydride, in the digestion. With the following charge:

- 0.5 gram substance
- 1.0 gram mercury (metal)
- 0.5 gram cupric sulphate (anhydrous)
- 2.0 gram phosphoric anhydride
- 1.0 gram sucrose
- 2.0 gram benzoic acid
- 20. cc. concentrated sulphuric acid,

a period of 60 to 80 minutes was required for digestion. Excellent results were obtained in determining the nitrogen content of alkaloids, inorganic nitrates, nitro compounds, and cyanogen derivatives. Equally good results were obtained when phosphoric anhydride was omitted from the charge, provided the period of digestion was lengthened to 3 to 4 hours. Pyridine and quinoline derivatives, azo compounds and inorganic nitrites gave low-values, even when oxidation by chromic acid or permanganate was resorted to, when the quantity of sucrose or of benzoic acid

was increased, or when benzoic acid was replaced by phenols, sulphonic acids or cellulose.

Gunning (30) recommends the digestion of 0.5 to 1 gram of substance with 20 to 30cc. of a solution of one part of potassium sulphate in two parts of ordinary sulphuric acid, until a colorless solution is obtained, requiring from one-half to two hours. He points out that acid potassium sulphate forms and acts upon the nitrogenous compound during the digestion exactly as would sulphuric acid heated under pressure above its boiling point. In the older methods sulphur trioxide might escape; here it is fixed and only water may escape; the sulphuric acid is concentrated, not weakened during the digestion. Gunning applied the method with success to such substances as morphine, antefebrein, peptone, bread, beer, milk and linseed cake.

Arnold and Wedemeyer (31) combined the Arnold and Gunning methods. They used:

- 0.5 gram substance
- 15. to 25 gram potassium sulphate
- 1. gram mercuric oxide
- 1. gram cupric sulphate
- 30. to 50. grams sulphuric acid,

and succeeded in converting into ammonia the nitrogen content of a number of compounds with which all other modifications of the Kjeldahl method are unavailable, e. g. quinoline and pyridine compounds, provided the bodies in question be non-volatile below the boiling point of sulphuric acid. When several nitrogen atoms are present in the heterocyclic ring, the ease or difficulty of converting the total nitrogen content into ammonia may depend upon whether the nitrogen atoms be adjacent to or distant from each other. The former class of compounds seems to be more difficult to convert into ammonia, as is shown by experiments on members of the pyridazin, pyrimidin, pyrazin, quinazolin, cinnolin, quin-oxalin, pyrazol and pyrazolin groups. In general, if the simple Kjeldahl treatment yield a lower percentage of nitrogen in a compound than does this modification, then nitrogen is contained in the ring. Certain determinations made by this method on anti-pyrine show that one at times may obtain concordant results and, therefore, apparently correct analyses by preserving the same conditions, while in reality the results are too low. These investi-

gators noticed that, if granulated zinc be replaced by two to three grams of zinc dust of known nitrogen content in the distillation, the use of potassium sulphide is unnecessary.

Winton, Ogden and Mitchell (32) applied the method of Arnold and Wedemeyer in determining the nitrogen content of both white and black peppers, and of their ether extract. They direct that—

- 1 gram substance
- 1 gram cupric sulphate
- 1 gram red mercuric oxide
- 15 to 18 grams potassium sulphate
- 25 cc. sulphuric acid

be heated gently until foaming ceases, then boiled from 3 to 4 hours. Before making alkaline in the distillation, 50cc. of potassium sulphide solution are added. Pure piperine gave results correct to within a tenth of one per cent.

Krüger (33) introduced potassium bichromate as the oxidizing agent in the digestion. From 0.2 to 0.8 gram of substance is dissolved in 20cc. of concentrated sulphuric acid with the aid of gentle warming, if necessary. After the solution has cooled, finely powdered bichromate is added in portions of 0.5 gram until 0.5 gram has been added in excess of the quantity theoretically required for complete oxidation of the substance. If carbon dioxide be evolved, even in the cold, addition of further quantities of bichromate must be deferred until the gas evolution ceases. Otherwise the entire quantity of bichromate may be added at once. The flask is next placed in a cold water bath, which is then heated. When the water boils and all the bichromate has dissolved, the flask is heated for ten minutes, with frequent shaking, upon a wire gauze, over a small flame, which need but touch the gauze. The end of the operation is recognized by the pure green color of the solution and the cessation of the evolution of gas. Frequently toward the end of the process chromic salts separate and cause the liquid to bump. Krüger states that the method yields good results with members of Dafert's first class of compounds (9). Several experiments on members of Dafert's second group lead to negative results, although the application of the method to this group is still a field for research.

Dyer (34) gently heats 0.5 to 5.0 grams of material with 20cc.

of strong sulphuric acid and a single drop of mercury until initial vigorous action has ceased, then gradually increases the heat during a period of 10 to 15 minutes, until brisk boiling begins. Ten grams of potassium sulphate are added and digestion is continued for 30 to 60 minutes when the contents of the flask become clear and colorless. For nitrates the use of phenol or, preferably, salicylic acid, zinc dust and mercury is recommended. Results are given of the analysis of a large number of aliphatic and aromatic compounds as well as cyanogen derivatives and alkaloids. Sucrose and zinc dust aided in the reduction of many refractory compounds.

Riviere and Bailhache (35) report the result of certain experiments designed to shorten the time required for decolorization with sulphuric acid in the digestion. Various substances, such as iron sulphate, vanadic, boric, molybdic and arsenic acids, were used to raise the temperature of the sulphuric acid, but in each case where the results were correct the process was too slow. Substitution of phosphoric acid for sulphuric acid yielded unsatisfactory results, even when manganese dioxide and phosphate were added to the charge. Ferric oxide and phosphoric acid gave correct results; however, the method is slower and more unpleasant than that of Kjeldahl. The only objection to the Gunning method is the relatively long time required with some substances, such as horn, for complete conversion of the nitrogen into ammonia. In the Kjeldahl method loss of nitrogen occurs if a great excess of mercury be used, and the mercury must be precipitated before distilling. Correct results were obtained with the greatest speed by digesting with sulphuric acid and 1 to 2 grams of sodium pyrophosphate for from 1 to 2 hours.

Dakin (36) directs that the substance be heated with the ordinary mixture of potassium sulphate and sulphuric acid to thorough disintegration, then allowed to cool below 100°C. A few grams of potassium persulphate are added and heating is resumed; vigorous evolution of oxygen occurs, and the black solution becomes clear. If the reaction appears incomplete, heat further, cool and add more persulphate. The persulphate must not be added to the liquid at too high a temperature; otherwise the salt will decompose too rapidly and proper oxidation will not occur. The function of the persulphate is twofold; it acts as an oxidizer and at the same time strengthens the sulphuric acid. Good results were ob-

tained more quickly with difficulty decomposable bodies like acetanilide, sulphanilic acid and the alkaloids by this method than by other methods. Dakin sums up: "It would appear that in the case of substances which are difficult to completely decompose in the ordinary way, potassium persulphate will find a useful application."

Recently the Gunning method has been modified by addition of a slight quantity of cupric sulphate to hasten the digestion. The Association of Official Agricultural Chemists (37) are considering the modification of the official method by permitting the addition of 0.1 to 0.3 gram of the crystallized salt. Hawk (38) reports that nitrogen is always lost whenever more than 0.2 gram of cupric sulphate is used in a digestion.

EXPERIMENTAL WORK ON ANTIPYRINE.

But one series of determinations of the nitrogen content of antipyrine—dimethylphenylpyrazolon—by any modification of the Kjeldahl method is to be found in the literature. Arnold and Wedemeyer (31) obtained the following results by their method:

Weight of Antipyrine used in grams.	Period of Digestion.	Per cent. of Nitrogen obtained.
0.7075	2 1/2 hours	9.6
0.6221	1/2 hour	9.69
0.658	5 hours	12.90
0.4356	2 hours	9.52

In the last experiment potassium permanganate was used for final oxidation. The results were not bettered by prolonging the digestion for 10 to 15 hours, or by subsequent oxidation with permanganate, barium dioxide, lead dioxide, or by the addition of phosphoric anhydride. A three to six fold increase of the cupric sulphate or mercuric oxide caused a loss of nitrogen. These results are considerably below the theoretic per cent., which is 14.89.

In the following experiments Jena flasks of 500cc. capacity were used for both digestion and distillation. The digested contents of each flask were dissolved in 200cc. of distilled water; a little granulated zinc was added, and an excess of concentrated sodium hydroxide solution (usually 100cc.) was poured in so that it sank beneath the solution of digested material. The flask was

connected with a safety bulb and a block tin condenser, and then the contents of the flask were mixed by shaking. To the lower end of the condenser was attached a piece of glass tubing of the same bore as the tin tube, for experience has shown that even acid of the dilution used will act upon tin and thus introduce an appreciable error. This glass tubing dipped beneath the surface of a measured quantity of $\frac{N}{10}$ sulphuric acid during the distillation proper, which was continued until bumping began, usually from 40 minutes to an hour. The Erlenmeyer flask, which contained the distillate, was then lowered so that the tubing was above the liquid, and the distillation was continued for 10 minutes, when the exterior of the tube was washed off into the flask and the contents were titrated with $\frac{N}{10}$ sodium hydroxide, using Grüber's congo red as an indicator. Whenever mercuric oxide was used in the digestion, the potassium sulphide solution was added and mixed by shaking before addition of the zinc and alkali. During several digestions, e. g. those according to Jodlbauer, and Riviere and Baillhache, it became necessary to add a slight amount of cupric sulphate to hasten the clearing of the liquid. Unless otherwise stated, the period of digestion was 5 hours. The antipyrine used was from two sources; one was a domestic brand, the other was the German "Löwenmarke." Both gave about the same percentage of nitrogen by the same method.

Antipyrine was digested with 0.7 gram of yellow mercuric oxide and 30cc. of concentrated sulphuric acid for 5 hours. No permanganate was used.

0.5235 gram antipyrine gave 11.52% N.

0.5224 gram antipyrine gave 11.52% N.

Samples were digested as above, and final oxidation was made with permanganate.

Permanganate was added to the hot digested material, which was again heated strongly.

0.5032 gram antipyrine yielded 10.22% N.

0.5038 gram antipyrine yielded 11.48% N.

The flask and its contents were cooled, permanganate was added, and heat was again applied.

0.5030 gram antipyrine yielded 9.90% N.

0.5124 gram antipyrine yielded 10.21% N.

Permanganate was added to the warm liquid, which was not again heated.

0.5201 gram antipyrine yielded 11.61% N.

0.5103 gram antipyrine yielded 11.87% N.

A saturated solution of permanganate in concentrated sulphuric acid was used as recommended by Czeczetka. However, use of a tap-funnel was replaced by a more convenient and less dangerous procedure. The solution in sulphuric acid was poured from a beaker down the side of the flask, then mixed by shaking with the cold solution which had been digested with mercuric oxide.

0.5161 gram antipyrine gave 12.46% N.

0.4888 gram antipyrine gave 12.31% N.

0.4557 gram antipyrine gave 11.97% N.

0.4581 gram antipyrine gave 11.99% N.

Samples were digested with 0.7 gram of crystallized cupric sulphate and 25cc. of a solution of 25 grams of phosphoric anhydride in 100cc. of concentrated sulphuric acid according to Wilfarth.

0.5074 gram antipyrine gave 9.62% N.

0.5037 gram antipyrine gave 9.80% N.

Wilfarth's newer method was also followed. Antipyrine was digested with 0.7 gram of mercuric oxide, 18cc. of concentrated and 12cc. of fuming sulphuric acid.

0.5076 gram antipyrine gave 11.70% N.

0.5029 gram antipyrine gave 11.61% N.

The charge directed by Jodlbauer was used with the addition of 0.2 gram of crystallized cupric sulphate.

0.5259 gram antipyrine gave 10.75% N.

0.5091 gram antipyrine gave 11.16% N.

A sample of antipyrine was permitted to stand over night in contact with 1 gram of salicylic acid and 30cc. of concentrated sulphuric acid; then 5 grams of sodium thiosulphate were added and heat was applied for five minutes. Ten grams of potassium sulphate and 0.2 gram of cupric sulphate were added and the digestion was continued for 5 hours.

0.5010 gram antipyrine yielded 12.11% N.

Two determinations were made by the original method of Arnold with the following charge:

- 1.1 gram mercuric oxide
- 0.7 gram crystalline cupric sulphate
- 2.0 gram phosphoric oxide
- 1.0 gram sucrose
- 2.0 gram benzoic acid
- 30. cc. concentrated sulphuric acid.
- 0.5216 gram antipyrine yielded 10.12% N.
- 0.5406 gram antipyrine yielded 10.07% N.

The official Gunning method required 5 hours to produce a clear solution; digestion was continued for an extra hour with this result:

- 0.5011 gram antipyrine gave 12.26% N.
- 0.5043 gram antipyrine gave 12.68% N.

The official Gunning method, modified by addition of cupric sulphate, was also tried.

- With 0.1049 gram cupric sulphate
- 0.5026 gram antipyrine gave 11.48% N.
- 0.2003 gram cupric sulphate
- 0.5234 gram antipyrine gave 11.24% N. ,

When the method of Arnold and Wedemeyer was tried with a charge of 1 gram each of mercuric oxide and cupric sulphate, 16 grams of potassium sulphate and 30cc. of concentrated sulphuric acid,

- 0.5650 gram antipyrine gave 10.70% N.
- 0.5025 gram antipyrine gave 10.43% N.

The bichromate process of Krüger produced the lowest results of the series.

- 0.2341 gram antipyrine yielded 2.45% N.
- 0.5053 gram antipyrine yielded 1.57% N.

Dyer's process was applied using 30cc. of concentrated sulphuric acid and substituting 0.7 gram of mercuric oxide for metallic mercury.

- 0.5097 gram antipyrine yielded 11.69% N.
- 0.5169 gram antipyrine yielded 11.79% N.

In digesting according to Riviere and Bailhache, 30cc. of concentrated sulphuric acid, 2 grams of sodium pyrophosphate and 0.1 gram of cupric sulphate were used.

0.4706 gram antipyrine yielded 13.47% N.

0.4899 gram antipyrine yielded 13.20% N.

Weighed samples of antipyrine were allowed to stand over night with 5 grams of stannous chloride and 30cc. of concentrated sulphuric acid. Heat was then applied for 10 minutes; 10 grams of potassium sulphate and about 0.1 gram of cupric sulphate were added, and the digestion was continued for 5 hours.

0.4380 gram antipyrine gave 12.62% N.

0.4768 gram antipyrine gave 12.87% N.

An experiment was made using lead peroxide as the oxidizing agent; 0.5104 gram of antipyrine, 8.5 grams of the peroxide and 30cc. of concentrated sulphuric acid were digested for 5 hours. Only 10.20% of nitrogen was obtained.

When the following determinations according to Dakin were made, the potassium persulphate added to each flask was accurately weighed and due allowance was made in the calculation for the nitrogen content of the salt.

0.5256 gram antipyrine gave 12.21% N.

0.5074 gram antipyrine gave 12.33% N.

Sodium peroxide was substituted for the potassium persulphate with this result:

0.5108 gram antipyrine gave 13.25% N.

CONCLUSIONS.

Antipyrine has been digested in sulphuric acid solution with various combinations of the following reagents:

Catalysers—Cupric sulphate, mercuric oxide, platinic chloride.

Oxidizing Agents—Lead dioxide, sodium peroxide, potassium persulphate, potassium dichromate.

Reducing Agents—Sodium thiosulphate, stannous chloride, sucrose, phenol, organic acids.

Compounds which elevate the boiling point of the solution—Phosphoric anhydride, potassium sulphate, sodium pyrophosphate.

In no case has the theoretic per cent. of nitrogen been obtained;

the lowest values were obtained by use of potassium dichromate, the highest results by use of sodium peroxide, or of sodium pyrophosphate and cupric sulphate. The series of results obtained by digestion of antipyrine with mercuric oxide with and without subsequent oxidation by means of potassium permanganate are of interest. When heat was applied after the addition of permanganate, a lower percentage of nitrogen was obtained than when no permanganate was used. On the other hand, when permanganate was added and the digested material was not again heated, a higher percentage of nitrogen was obtained than when the use of permanganate was omitted.

The low values obtained are due either to incomplete oxidation of the antipyrine to ammonia and oxides of carbon or to escape of nitrogen in the elementary state. Since antipyrine-p-sulphonic acid exists, and since antipyrine also possesses the properties of a mono acid base (39), it must be retained in solution by the sulphuric acid and cannot escape from the flask unchanged during the digestion.

The absolute method of Dumas may be applied to antipyrine with success as is shown by the following determination made in the course of this investigation:

0.4319 gram of antipyrine gave 57.3cc. of nitrogen gas, which was measured at 25.6°C. when the pressure of the atmosphere was 761.0 m.m. of mercury. The percentage of nitrogen was 14.73, while the theory calls for 14.89%.

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THE Maschinenbau-Actien-Gesellschaft, Hanover, Germany, has now delivered the 5000th locomotive built at its works, and a summary is published of the work done in the locomotive department since the works were founded, in 1835. Of the 5000 locomotives constructed 1100 were for railroads outside of Germany, of which 241 went to Russia, 115 to Roumania, Japan coming next with 93, and 14 for the Argentine, the remainder being divided between European and Asiatic countries, and six to Chile. The especially interesting remark is made that none of these engines was sent to the United States.—*Iron Age*.