probably a much higher occurrence of carbonate than would be found in virgin or cultivated calcareous soils adapted to plant growth. In cases of soils running over 15 per cent CaCO_3 , it would be well, probably, to increase the strength of acid to 1/5.

Two soils treated with an exceedingly insoluble dolomite to the amount of chemical equivalence of 200,000 pounds of CaO per two million pounds of soil gave the following results:

PER CENT CaCO_3 in	Soil A	Soil B	Av.
Boiled, minus boiling blank on original soil.....	13.69	14.21	13.95
1/5 HCl, room temp., 30 min. agitation and aspiration.....	13.80	14.10	13.95

As emphasized by italics in *Bulletin 100*, we were able to secure by the use of 1/15 phosphoric acid complete decomposition of a very insoluble dolomite, when it was EXCEEDINGLY FINE. It would not be feasible, however, to grind all miscellaneous and unknown soils to such fineness as would be essential, in order to insure complete decomposition by 1/15 H_3PO_4 of a possible exceptional occurrence of dolomite. For this reason, together with the substitution of the absorption tower for the gravimetric procedure, we modify the method by the suggestion that 1/10 HCl be used for miscellaneous work.

Instances where considerable residual magnesite might be expected to occur in soils would be exceedingly rare. We should probably note, however, that we have found that in such cases neither the old procedure of boiling for one minute or several minutes, nor the Marr method, nor the Tennessee Station method will effect the complete decomposition of the mineral magnesium carbonate. In soils treated excessively with magnesite at this Station, we found it essential that boiling be continued during the 30-minute period of aspiration in order to decompose completely all of the magnesite.

MANIPULATION OF MODIFIED PROCEDURE

Twenty-five cc. of approximately 4 per cent NaOH solution are placed in each absorption tower, and CO_2 -free distilled water added to cover the beads. The suction, which is applied before running the acid from the bulb of the inlet tube into the 300 cc. Erlenmeyer soil-container flask, is controlled by screw corks on the rubber tubing to better advantage than by use of the metal stopcocks of the suction system. After agitation and aspiration for 30 minutes, the caustic is drawn out of the towers into glass tumblers and the towers are completely filled with CO_2 -free water. After this washing has been drawn the tower should be rinsed several times. The NaOH solution is then titrated almost to a disappearance of the color given by one cc. of phenolphthalein, by the use of approximately normal sulfuric or nitric acid and the red color is then completely removed with the standardized weaker acids, $N/2$ and $N/20$. Two drops of methyl orange are then added and the CO_2 is determined by titration to the end point of methyl orange. For the average soil the entire methyl orange titration is carried out by the use of $N/20$ acid, but with excessive CO_2 occurrences, it is convenient to use $N/2$ acid to the near end point, and the titration is then completed with $N/20$ acid, which has a CO_2 value of 0.0022 g.

per cc. In determining the blank on the NaOH we also include the atmosphere blank of the apparatus. This atmosphere blank is usually exceedingly small and constant, and its use eliminates the necessity of sweeping the apparatus free of CO_2 before making determinations. For the average soil 20-gram charges should be used and 60 to 75 cc. of 1/10 acid added for decomposition of the carbonates. A nitrogen bulb should be inserted as a trap between the bottle containing NaOH for purification of incoming air and the acid bulbs of the apparatus.

A CORRECTION

As above stated, it was found that it is necessary to have dolomite in the form of a floury powder in order to insure its complete disintegration by 1/15 phosphoric acid and in the original CO_2 determinations upon the dolomite used for treatments, the analyses of which were given in Table V, Tennessee Station, *Bull. 107*, the analyzed samples were so conditioned. However, in the supplementary determination for residual CO_2 in the field samples reported in Table VI of that bulletin the soil samples were ground to pass a 100 mesh sieve.

Upon recently submitting the composites of these two sets of eight soils each to boiling and applying the boiling blank of the untreated soil, 0.441 per cent of CO_2 was found in the limestone residues while 0.450 per cent was obtained from residual dolomite. The same composite soils, when analyzed by the use of 1/10 HCl at room temperature, gave 0.481 and 0.490 per cent of residual CO_2 for limestone and dolomite treatments, respectively. This means that the results for residual carbonates of dolomite treatment given in Table VI of *Bulletin 107* are erroneous, in that they are too low as a result of insufficient fineness of samples. All of the other tables of the residual carbonates, however, were verified by boiling and applying the boiling blank prior to the publication of the data.

The writers would qualify their previous conclusions, then, as to the complete disappearance of the magnesium carbonate of the COARSELY GROUND dolomite in the short length of time given. The general principle, however, is unaltered, as relating to the unusual affinity of magnesium carbonate for siliceous substances. And the corrected results for the residual carbonates indicated that the greater affinity between magnesium carbonate and silicates has offset to an extent the lesser solubility of the dolomite in carbonated water, as compared to the greater solubility of limestone.

DEPARTMENT OF CHEMISTRY AND AGRONOMY
UNIVERSITY OF TENNESSEE EXPERIMENT STATION
KNOXVILLE

THE CHEMISTRY OF BASE GOODS FERTILIZER

By ELBERT C. LATHROP
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INTRODUCTION

Although it has been long recognized that organic matter is a necessity for soil fertility, it is but lately that the deeper significance of soil organic matter in

relation to the complex problems of the soil and of the crop production has become apparent. Investigations have shown that the organic compounds in soils not only affect the physical conditions and chemical reactions of the soil but that they are also directly connected with fertility or infertility, some of them being essentially beneficial to the growth of plants while others are distinctly harmful. Of the organic compounds thus far isolated from soils, a large number contain nitrogen, and of these nitrogenous substances, some have been found rather widely distributed in soils varying as to location, climate, methods of cropping, etc. These nitrogenous compounds either occur as plant constituents or arise from the decomposition of plant or animal protein, brought about by the various biological and biochemical agents in the soil. Not only compounds of this class found in soils but also many other protein decomposition products have been studied, both alone and in conjunction with the three fertilizer elements, in respect to their action on plant growth, and they have been shown in a number of cases to exert a beneficial influence; furthermore, these complex compounds are available for use by the plant without first being changed by chemical or biochemical means into ammonia and then to nitrates.¹

That these facts have an immense practical bearing on fertilizers and the fertilizer industry, both from the standpoint of the producer and of the consumer, is at once obvious. The consumer of commercial organic fertilizers should be concerned not alone with the availability of the nitrogen in fertilizer but also in knowing the nature of the organic compounds he is adding to his soil and in understanding the physiological effect of these on plant growth, whether their action will be harmful or beneficial or a balance of these two effects. A chemical investigation of some of the types of commercial organic fertilizers with the view of determining the kinds and nature of the organic compounds in the fertilizer is therefore of interest to the agriculturist. The old high-grade nitrogenous fertilizers, such as cottonseed meal, dried blood, fish scrap, etc., are being used more and more for feed purposes, and the time cannot be far distant when their use as fertilizers will cease to be economic; thus a necessity for other and cheaper fertilizers of this type arises. On the market are a large number of fertilizers which may be characterized as "processed," *i. e.*, the crude materials, not in themselves permissible as fertilizers, are made to undergo some decided chemical change to render them suitable as plant nutrients. It has been found that the "availability" of the crude substances is nearly always greatly increased by such processing and that a much larger percentage of the nitrogen in the finished product is soluble in water, although the actual chemical changes produced seem to have received little attention. The chemical compounds in process fertilizers which are here shown to have direct fertilizer

significance have not been determined, other than to show that ammonia is formed during processing and that ammonia is more readily produced from the processed goods.

Since the wastes from which this type of fertilizer is made contain more or less protein, or protein-like substances, it seemed quite obvious that the finished fertilizers must contain more or less of the chemical compounds which would arise from pure proteins by similar treatment in the laboratory. As the action on plants of many of this class of compounds has been determined it is evident that the finding of such compounds in the fertilizers would throw much light on the question of the "availability" of the nitrogen in the fertilizer itself.

BASE GOODS A TYPE OF PROCESSED FERTILIZER

For a chemical study of processed fertilizers a sample of "wet-mixed" or "base goods" fertilizer was chosen as a representative of this type of fertilizer material. The base goods was obtained directly from the factory for use in this investigation. This fertilizer is made by the treatment of various trade wastes and refuse, such as hair, garbage tankage, leather scraps, etc., with rock phosphate and the requisite amount of sulfuric acid. These materials are mixed together in a "den" and the resulting mass is allowed to stand for several days, or until it is cool enough to be conveniently handled. In the course of the reaction the mass reaches a temperature approximating 100° C., and the identities of the original substances are almost or entirely lost. Under these conditions it is certain that more or less hydrolysis of the proteins in the crude materials takes place, with the formation of proteoses, peptones, polypeptides, or the simple amino acids, the kinds and number of products formed necessarily depending on the proportion of the different proteins in the original materials, on the amount and strength of the acid, the length of time of the reaction, and the temperature reached during the treatment.

Hartwell and Pember¹ have recently made a study of base goods in order to determine the availability

TABLE I—PERCENTAGE TOTAL NITROGEN IN CRUDE MATERIALS AND FINISHED PRODUCT (HARTWELL AND PEMBER)

Hair tankage.....	6.28	Base goods, including the above....	1.68
Roasted leather.....	6.49	Water-soluble nitrogen in base goods	1.28
Garbage tankage....	2.87	Water-insoluble nitrogen in base goods.....	0.40

TABLE II—PERCENTAGE OF THE TOTAL NITROGEN PRESENT IN DIFFERENT FORMS (HARTWELL AND PEMBER)

	Before put into den	After removing from den
In ammonia.....	6.5	14.3
In water-soluble organic matter.....	7.8	57.7
In water-insoluble organic matter.....	85.7	28.0

of the nitrogen contained compared with that of the high-grade nitrogenous fertilizers. The product they used was made from hair tankage, garbage tankage, and roasted leather, together with rock phosphate and sulfuric acid. Tables I and II give their figures for the analysis of the crude materials used in producing the fertilizer and of the finished product.

The experimental work of the present investigation was along two separate lines:

¹ THIS JOURNAL, 4 (1912), 441.

¹ "A Beneficial Organic Constituent of Soils: Creatinine," Oswald Schreiner, E. C. Shorey, M. X. Sullivan and J. J. Skinner, *Bull.* 83, Bur. Soils, U. S. Dept. Agr., 1911. "Nitrogenous Soil Constituents and their Bearing on Soil Fertility," Oswald Schreiner and J. J. Skinner, *Bull.* 87, Bureau of Soils, U. S. Dept. Agr., 1912.

I—Analytical, involving total nitrogen determinations and the separate estimation of the various forms in which nitrogen may occur.

II—A determination of the definite chemical compounds present in the fertilizer by suitable methods of isolation and identification.

THE CHEMICAL CHANGES INVOLVED IN PROCESSING

It is not the purpose of the present paper to enter in detail into the methods used in the chemical examination of the base goods. For the analytical study of the forms of nitrogen in the base goods the method of Van Slyke¹ was used in its essential details, omitting the determination of cystine, since the method for its determination is not applicable in this case.

It should also be stated that, although the results from the Van Slyke analysis are expressed in the usual way, arginine nitrogen, histidine nitrogen, etc., it is not intended to convey the impression that these fractions contain pure arginine, histidine, etc., since, as will be shown later, other compounds are included under these analytical terms. However, the nitrogen so expressed is that contained in compounds which give the various reactions upon which the Van Slyke method depends.

The analytical figures obtained by this method appear in Table IV and will be discussed after the isolation of certain of the constituents has been presented.

The method used for isolating and identifying the various organic compounds are such as have been used in this laboratory in separating these compounds from soils and are described in various publications from this laboratory.²

Since this investigation aims only at an explanation and exposition of the general chemical principles involved in the treatment of trade wastes and other organic material to render the nitrogen contained therein more available for agricultural purposes, it does not aim to present the research methods here employed as general methods for analyzing such fertilizers. Nor can the quantitative figures obtained be expected to apply to all products of similar manufacture, for the reason that the different kinds of nitrogen compounds will necessarily show different proportions according to the nature of the materials which enter into the mixture.

The compounds which were isolated from the base goods are tabulated in Table III according to the sources from which they have been derived and the chemical groups to which they belong.

TABLE III—ORGANIC COMPOUNDS ISOLATED FROM SAMPLE OF BASE GOODS

Arginine.....	Diamino acids or hexone bases	Products of protein hydrolysis by acid treatment of raw materials.
Histidine.....		
Lysine.....		
Leucine.....	Monoamino acids	Plant constituent, or product of hydrolysis of nucleoprotein.
Tyrosine.....		
Guanine.....	Purine base	Plant constituent, or product of conversion of nucleoprotein-base.
Hypoxanthine..	Purine base	

Establishing the presence of these products of acid hydrolysis of proteins, namely, the diamino acids,

¹ *J. Biol. Chem.*, **10** (1911), 15-55.

² Oswald Schreiner and E. C. Shorey, *Bur. Soils, U. S. Dept. Agr.*, 1910; Oswald Schreiner and E. C. Lathrop, *Bull.* **80**, *Bur. of Soils, U. S. Dept. Agr.*, 1911; E. C. Shorey, *Bull.* **88**, *Bur. Soils, U. S. Dept. Agr.*, 1913; Oswald Schreiner and E. C. Lathrop, *Bull.* **89**, *Bur. Soils, U. S. Dept. Agr.*, 1912; E. C. Lathrop, *Bull.* **158**, *U. S. Dept. Agr.*, 1914.

arginine, lysine, and histidine, and the two mono-amino acids, leucine and tyrosine, in the amounts in which they were found is of itself sufficient evidence to demonstrate that by the acid treatment of the crude materials used in the manufacture of the base goods the proteins contained therein have been changed. The change is shown to be a deep-seated one, since five of the compounds known to be final products of protein hydrolysis by acids are found. This, however, cannot be taken to mean that the proteins have been completely hydrolyzed by the acid treatment since it is possible to have present in the product of partial hydrolysis of proteins, not only the diamino and monoamino acids, but also such intermediate compounds as polypeptids, peptones, proteoses, etc.

In this connection the results obtained by use of the Van Slyke method, and given in Table IV, are of particular interest. For the nitrogen partition two samples of base goods were extracted: (1) with boiling water and (2) with boiling acid. In the former case only slight further hydrolysis of the materials in the base goods is to be expected since the free acid in the fertilizer is extremely weak, and the boiling temperature, 100° C., is that which was reached in the process of manufacture. In the case of the second extract complete hydrolysis of all the proteins or protein-like materials is certainly to be expected, since in addition to the original hydrolysis the material was boiled with strong hydrochloric acid for 24 hours, a treatment sufficient for the complete hydrolysis of most proteins. The differences in the results obtained from the analyses of the two extracts may, therefore, be expected to throw some light on the question of the completeness of hydrolysis of the original proteins by the acid processing.

TABLE IV—NITROGEN FORMS AS DETERMINED BY THE VAN SLYKE METHOD
Results expressed in per cent of

EXTRACT	Base goods		Total N in base goods	
	H ₂ O	HCl	H ₂ O	HCl
Total nitrogen.....	1.610	1.610	85.24(a)	88.64
Total soluble nitrogen.....	1.372(a)	1.435	14.76(a)	11.36(a)
Total insoluble nitrogen.....	0.238(a)	0.175(a)	23.23	23.70
Amide nitrogen.....	0.374	0.382	1.95	4.61
Amino nitrogen.....	0.031	0.074	6.89	6.46
Diamino { Arginine N.....	0.111	0.104	7.26	4.38
acid { Histidine N.....	0.081	0.070	5.06	7.26
fraction { Lysine N.....	0.081	0.117	33.75	33.92
Monoamino acid { Amino N.....	0.543	0.546	7.10	8.27
fraction { Nonamino N.....	0.114	0.133		

(a) Obtained indirectly.

Without discussing the significance of all the figures obtained by the use of this method it is interesting to note that the differences between the water extract and hydrochloric acid extract indicate the presence in the base goods of a nitrogenous compound not yet completely hydrolyzed.

In order to prove the presence of some intermediate product of protein hydrolysis, which is thus indicated by analytical methods, an aqueous solution of about 2.5 lbs. of base goods was made and the diamino acids were precipitated with phosphotungstic acid in the presence of 5 per cent sulfuric acid. The precipitate which formed was allowed to stand over night and after filtering off it was washed well with 5 per cent sulfuric acid and dissolved in sodium hydroxide. The phosphotungstic acid was then precipitated by adding barium hydroxide solution, and after filtering, the excess of barium was removed by adding sulfuric

acid until a neutral reaction was obtained. Portions of this solution were tested for peptones, proteoses, etc., with the following results: (1) The biuret test was positive; (2) a precipitate was obtained on saturation of the solution with ammonium sulfate, or with sodium chloride; (3) when the filtrate from the latter solution was treated with acetic acid a cloudy precipitate developed; (4) precipitates were also obtained with sulfuric acid, hydrochloric acid, phosphomolybdic acid and with phosphotungstic acid; (5) a precipitate was formed in the addition of alcohol to the solution. This precipitate was filtered off, dissolved in dilute alkali, and on addition of very dilute copper sulfate solution the biuret reaction was again obtained. These reactions are those which are given by proteoses and by the proteins and confirm the conclusions arrived at from the results with the Van Slyke method. The Millon reaction and the Hopkins-Cole reaction were both negative, showing the absence from this protein-like compound of the tyrosine and the tryptophane radicals.

A very large number of compounds intermediary between the protein and its primary hydrolysis products may occur, depending on a great variety of conditions, so that the actual identification of the compounds under discussion would be a difficult matter. However, the nature of this compound may be approximately determined by the results obtained in the study of the two extracts by the Van Slyke method. These results indicate the presence in the base goods of a compound of a proteose nature, which, since it gives a biuret test, must be composed of at least three amino acids. The results indicate still further that the compound is composed of acid amide radicals, diamino acids—particularly lysine, and monoamino acids—those containing amino nitrogen and especially those containing non-amino nitrogen. Since the figures obtained by the nitrogen partition method are subject to a certain amount of error when applied to such a mixture the figures can be taken as only approximate for the various forms of nitrogen which make up this compound.

In Table V are given the primary hydrolysis products of a number of proteins which may be present in the base goods. These results were obtained by the esterification method and show how the different proteins vary in the nature and amount of the units composing them. Many monoamino acids, besides leucine and tyrosine, occur in these proteins, and there must consequently be present in the base goods amino acids other than the two isolated. This is apparent from the composition of the various proteins shown in the table. Owing to the large amount of amide nitrogen present in the fertilizer, which was split off by the acidulation of the original proteins of the trade wastes, it may be concluded that considerable quantities of aspartic or glutamic acids are present in this sample of base goods.

The conclusion to be drawn from the results obtained by the examination of this fertilizer by means of the analytical and isolation methods are as follows: The process by which the nitrogen of certain

trade wastes, such as hair, lather, garbage, etc., is made more available, is recognized as a process of partial hydrolysis of the complex protein contained in such materials, resulting in ammonia, amino acids, etc., all of which are more available than the original

TABLE V—PRODUCTS OF ACID HYDROLYSIS OF VARIOUS PROTEINS

COMPOUND	"Synotin"	"Keratin" from				"Leg-amin"
	from cattle flesh (a)	sheep's horn (b)	sheep's wool (b)	horse's hair (c)	Hali-but muscle (d)	Ox from pea (e)
Glycine (g)	0.5	0.5	0.6	4.7	0.0	2.1
Alanine (g)	4.0	1.6	4.4	1.5	(?)	3.7
Valine	0.9	4.5	2.8	0.9	0.8	0.8
Leucine (g)	7.8	15.3	11.5	7.1	10.4	11.7
Isolencine						8.0
Phenylalanine (g)	2.5	1.9		0.0	3.1	3.2
Tyrosine (g)	2.2	3.6	2.9	3.2	2.4	2.2
Serine		1.1	0.1	0.6	(?)	(?)
Cystine		7.5	7.3	8.0		0.5
Proline	3.3	3.7	4.4	3.4	3.2	5.8
Oxyproline						3.2
Aspartic acid (g)	0.5	2.5	2.3	0.3	2.8	4.52
Glutamic acid (g)	13.6	17.2	12.9	3.7	10.1	15.5
Tryptophane					(+)	(+)
Arginine (g)	5.1	2.7		4.5	6.4	7.5
Lysine (g)	3.3	0.2		1.1	7.5	7.6
Histidine (g)	2.7			0.6	2.6	1.8
Ammonia (g)	0.9				1.4	1.1
	47.3	62.3	49.2	39.6	50.7	67.5
						62.4

(a) Abderhalden and T. Sasaki, *Z. physiol. Chem.*, **51** (1907), 404.

(b) E. Abderhalden and A. Voitinovici, *Ibid.*, **52** (1907), 348.

(c) E. Abderhalden and H. G. Wells, *Ibid.*, **46** (1905), 31; A. Argiris, *Ibid.*, **54** (1905), 86.

(d) T. B. Osborne and F. W. Heyl, *Am. J. Physiol.*, **22** (1908), 433.

(e) T. B. Osborne and D. B. Jones, *Ibid.*, **24** (1909), 437.

(f) T. B. Osborne and F. W. Heyl, *J. Biol. Chem.*, **5** (1908), 197.

(g) Physiological action on plant growth has been determined and reported in *Bull.* **87**, Bureau of Soils, U. S. Dept. Agr.

protein material; this hydrolysis is almost complete, the nitrogenous compounds formed being principally the primary products of protein hydrolysis, together with a small amount of proteose-like compound which has not been fully decomposed.

AVAILABILITY OF THE NITROGEN OF ORGANIC FERTILIZERS

The question of the availability of the different kinds of nitrogen contained in organic fertilizers is one that has caused considerable discussion. A number of methods have been proposed for determining this factor, and while some of them give helpful results, all except the plant method are open to more or less objection, since the methods are empirical and the nature of the complicated compounds in which the nitrogen is linked in the fertilizer is unknown or only guessed. When these nitrogen compounds are known and their action on plants, as well as the action of the compounds formed from them during their decomposition in the soil, have been determined, then the question of the availability of the nitrogen of organic fertilizers can be understood. Originally it was held that plants were able to use nitrogen only when it was offered to them in the form of nitrates; this idea, however, was modified when it was discovered that under certain conditions plants used ammonia or ammonium salts without their conversion into nitrates quite as well as they used the nitrates themselves. During the past few years it has been clearly demonstrated that plants use nitrogen not only in the form of nitrates and ammonia but in the form of complex organic compounds.¹ The action of a number of these nitrogenous compounds has been tested in this laboratory in conjunction with the three fertilizer elements and it has been found that in some cases

¹ Hutchinson and Miller, *Centr. Bakt. Parasitenk.*, **30** (1911), 513; Schreiner and Skinner, *Bull.* **87**, Bureau of Soils, U. S. Dept. Agr., 1912.

the nitrogen compounds are not only used as a source of nitrogen for the growing plant, without any change in the compound, but that they are apparently nitrate spacers, *i. e.*, the plant uses them in preference to the nitrates. Instead, then, of only one kind of nitrogen compound, *nitrate*, or at most two, *nitrate* and *ammonia*, there appear to be a very large number of nitrogenous compounds which have properties of physiological importance to plant growth. The question of the availability of nitrogen compounds can therefore be answered only when the nitrogen compounds contained in the fertilizer can be determined in amount and at the same time classified according to their physiological action on plant growth. It is hardly necessary to state that such a method does not exist at present and that the physiological action of only a part of the total number of nitrogenous compounds present in fertilizers is known.

The physiological action on plants of all of the nitrogenous compounds isolated from base goods has been determined by means of water cultures¹ and the results obtained may be stated briefly, as follows: Both of the purine bases are used by the plant as a source of nitrogen and are beneficial to plant growth; furthermore, the hypoxanthine acts as a nitrate spacer, there being less nitrate used by the plant in the presence of hypoxanthine than when the hypoxanthine is absent. Histidine, arginine, and lysine² are all beneficial to plant growth, causing nitrogen increases in the plant, and the two first diamino acids act as nitrate spacers; this may also be true of lysine, although this property of lysine has not been studied. Leucine is also beneficial to plant growth, but tyrosine, in the light of later investigations, is somewhat doubtful in action. Of the other monoamino acids which may be present in base goods, aspartic acid, glutamic acid, and glycocoll have been found to be beneficial. The action of alanine is somewhat doubtful, it apparently being beneficial in low concentrations, while phenylalanine is reported as harmful. Thus six of the seven compounds isolated from the base goods are actually available to plants as such and have a beneficial action. Of the monoamino acids, other than the two isolated from base goods, which have been studied in regard to their action on plant growth, three have been found to be beneficial, one doubtful, and one is reported as being harmful.

The high-grade nitrogenous fertilizers, such as dried blood, are considered to have a high availability owing to the fact that the nitrogenous materials when placed in the soil quickly undergo the process of ammonification and nitrification, the nitrogen thus being changed into a form which can be immediately used by the plant. In fact, Lipman³ has proposed a method for the determination of the availability of the nitrogen of organic fertilizers, depending on the amount of ammonia produced under certain conditions in a given length of time. It is evident from the above consideration that such a method does not tell the whole

story, since, in the decomposition of protein materials, such as dried blood, intermediate compounds are formed which are undoubtedly in themselves beneficial to plant growth. In order, therefore, to understand the complete action of the nitrogenous materials in the base goods it is necessary to know how the compounds contained in it are acted upon by ammonifying bacteria. Jodidi¹ has shown that the amino acids and acid amides are quite readily ammonified when placed in the soil, the rate of ammonia formation and the amount of ammonia formed depending apparently upon the chemical structure of the particular compound under consideration. In general, he found that the simpler the chemical structure of the nitrogen compound the more quickly and readily it was ammonified. In the light of these facts it appears that polypeptides, peptones, proteoses, and proteins would be ammonified still more slowly than the amino acids since their structure is increasingly more complex.

Hartwell and Pember² in their study on the availability of the nitrogen of base goods, by means of plant tests found that it had apparently as high an availability as dried blood, the water-soluble nitrogen having even a higher availability. From the nature and amounts of the compounds present in the base goods this might be predicted. In the case of the dried blood, the nitrogen is practically all in the form of complex protein material which must be broken down into simpler compounds by bacterial action, with the formation of ammonia and other nitrogenous compounds, some or all of which may be of physiological importance to plants. With the base goods the case is a little different; the greater part of the nitrogen is at once available for plant use, and at the same time these available compounds may be changed more easily and quickly by bacteria of the soil into ammonia and nitrate, which in turn are used by the plant. The soluble nitrogen of base goods should therefore be in a more readily available form than the nitrogen of dried blood or other nitrogenous fertilizers which are entirely of a protein nature.

THE CHEMICAL PRINCIPLES UNDERLYING THE UTILIZATION OF NITROGENOUS TRADE WASTES

It has already been stated that in order that the plant may make use of the nitrogen of even high-grade organic fertilizers, it is necessary for the proteins therein to be at least partially decomposable by the biological and biochemical agencies of the soil. The low-grade organic nitrogenous fertilizers resist decomposition by these biological and biochemical soil agencies, and their nitrogen is therefore considered to be less available for plant use. The guiding idea behind the processes proposed for the treatment of trade wastes, which will not decompose easily in the soil as such, is to change the nitrogen compounds contained in them in such a way that ammonia is formed and that their decay in the soil is more rapid.

Much of the nitrogenous materials in trade wastes is of a protein nature, since the products from which

¹ Bull. 87, Bureau of Soils.

² Unpublished data.

³ Lipman, Brown and Owen, *Centr. Bakt. Parasitenk.*, 31, II Abt. (1911-1912), 49-85.

¹ Research Bull. No. 9, Iowa Expt. Sta.

² Loc. cit.

FIG. I.—TANKS USED FOR STEEPING BARLEY SHOWING AIR LINES

offensive or disagreeable odors must also be avoided. The species of bacteria, moulds and wild yeast encountered in air are very many, but fortunately only five species of bacteria are dangerous in a brewery, *i. e.*, acetic, lactic, butyric, sarcinae or pediocci, and *Bacillus viscosus*. Practically all others, including all the common pathogenic bacteria, will not survive fermentation. This is very important from a sanitary standpoint.

In our plant we use air of different degrees of sterility,

FIG. II.—PERMANGANATE TANKS

depending upon the use to which the air is to be applied. All air used is drawn through a pipe line from the top of our highest building by means of a pump which compresses it and conveys it to the various points where it is needed.

and removed by an overflow device. The air used in this process is purified by passing it through a series of large drums filled with a solution of potassium permanganate. As the air is sprayed through these tanks of permanganate in a very fine spray the permanganate not only washes the air but oxidizes or removes any objectionable odors and also removes the greater part of the dust, dirt, and bacteria.

After being steeped for a certain length of time, the wet barley is conveyed to a series of compartments kept at a uniform temperature in order to allow the barley to grow. During this growth certain changes take place in the barley kernel, various enzymes, such as amylase and peptase, develop, and during the growing process large amounts of carbon dioxide and other gases are evolved. It is necessary to remove these gases and at the same time provide the barley with a fresh supply of oxygen. This is accomplished by means of air. This air is purified by passing it through a series of galleries constructed of perforated metal plates. Through the center and running the entire length of these galleries there is a water pipe equipped with a large number of very fine sprays. The air must pass through this fine spray of moisture. After the growing process is complete the barley or as it is now called, "green malt," is transported to kilns and dried. It is then cleaned and this represents the finished malt.

The third and perhaps the most important place that air is used is in the fermenting department. The green malt is mixed with water and an infusion made; this is finally boiled with hops and the resulting wort must then be cooled to the proper temperature at which the yeast is to be added for the fermentation by a series of coolers very similar in construction to the ordinary condensers used in the laboratory for distillation purposes. Air is passed through the wort when it is still hot. This air functions mainly as an oxidizing agent. The specific nature of this oxidation has not been very thoroughly investigated but it plays a very important rôle in the brewing process and serves to render certain constituents of the hop, commonly termed hop resins, insoluble; it also has some action on the proteins and carbohydrates at this high temperature.

After the temperature of the wort has been considerably reduced, more air is added, not as an oxidizing agent, but for solution by the cold wort. This dissolved air is necessary for the respiration and growth of the yeast.

When the wort has been cooled and the yeast added, more air serves merely to mechanically agitate the yeast and wort and secure a more or less uniform mixture.

by plants. The change

compounds has been brought about by the partial hydrolysis of the proteins contained in the various trade wastes used in the manufacture of the fertilizer. When proteins decompose through natural conditions, be they in the soil or out of it, a certain amount of hydrolysis of the proteins takes place and if the decomposition is allowed to proceed long enough under proper conditions complete hydrolysis will result.

The principle involved in making the nitrogenous material in the soil available and in increasing the availability of low-grade nitrogenous materials by factory treatment is therefore the same. In other words, the general chemical principle to be applied in making available the nitrogen of low-grade fertilizers, trade wastes, etc., is that of complete or partial hydrolysis by any suitable means of the proteins contained in the wastes. Partial hydrolysis of proteins may be accomplished by means of heat, boiling, steaming, heating under pressure; both partial and complete hydrolysis may be obtained by treating with strong acids or alkalis, either in the cold for a long time or heating to a high temperature, the extent of hydrolysis depending on the several conditions. An examination of the patent literature shows that all of these means have been proposed for the treatment of waste materials, although the actual chemical principle of hydrolysis involved in the treatment is not considered. Also, in a number of processes in actual use, various of these treatments are practiced, resulting in different degrees of hydrolysis of the original proteins. While the availability of the nitrogen of a fertilizer depends on the substances in which the nitrogen is contained, it also depends on the extent of hydrolysis of the proteins used in the manufacture. It may be stated that in general the more extended and final the hydrolysis the more available the nitrogen of the compounds formed, since, as has been shown, the final products of hydrolysis are utilized by the plants as such and are at the same time more readily changed into ammonia by bacteria, etc., than are the intermediate compounds produced by partial hydrolysis.

SUMMARY

The base goods used as a type of processed fertilizer

being principally the products of primary protein decomposition, together with a small amount of a proteose-like compound which has persisted.

From the sample of base goods were isolated the following nitrogenous compounds: two purine bases, guanine and hypoxanthine; the three diamino acids, arginine, histidine, and lysine; and two monoamino acids, leucine and tyrosine. A proteose-like compound was also obtained and its general nature established.

By means of the Van Slyke Method the approximate proportions of the different forms of nitrogen contained in the fertilizer were estimated, and the extent of the hydrolysis of the original proteins was determined. It was also shown by this method that the proteose-like compound was composed of acid amide radicals, diamino acid radicals, especially lysine, and monoamino acid radicals, particularly the monoamino acids which contain non-amino nitrogen.

The question of the availability of nitrogen is discussed, and from a consideration of the amount and the physiological action on plants of the different forms of nitrogen present in the fertilizer it is concluded that the water-soluble nitrogen of this fertilizer should have an availability equal to or greater than the nitrogen of dried blood, or other high-grade fertilizers. These results are in accord with the results obtained by the plant method of determining availability.

The general chemical principle which underlies the method for rendering available the nitrogen contained in most trade wastes, which are to be used as fertilizing materials, is shown to be either partial or complete hydrolysis of the protein of the wastes by any suitable means.

The more complete the hydrolysis the more available the nitrogen in the fertilizer becomes, since the products of complete hydrolysis of proteins are not only utilized by the plants themselves as nutrients but they are more easily ammonified when placed in the soil than are the more complex compounds, such as peptones, proteoses, and the proteins themselves.

BUREAU OF SOILS

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

LABORATORY AND PLANT

PURIFICATION AND STERILIZATION OF AIR¹

By S. BORN AND WM. F. CARTHAUS

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In considering the question of air, we have taken it up mainly from the standpoint of the fermentation

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industry, but the methods employed here could easily be extended to other fields such as the ventilation of hospitals, schools, public buildings and factories.

Air is one of the most important factors in the brewing process, and as sterile air can be obtained by none of the ordinary methods employed for purifying