position will show a very close agreement between "theoretical" and "actual" results. This indicates that "acid phosphate" and other ingredients are not "disturbing" factors and that the manufacturer having determined in advance the nitrogen activity of his crude stock may be assured of getting full credit for the nitrogen activity of his finished product.

ORGANIC AND VOLATILE MATTER.

A determination of the organic and volatile matter in the water insoluble portion of crude stock or a fertilizer will furnish a reliable clue to the character of the organic nitrogen in the material. The procedure in use at the Vermont Experiment Station laboratory is as follows: Weigh two grams of material onto a filter paper and wash with about 250 cc. of water at room temperature. Dry the residue at about 80° C. and transfer from the filter to a small tared porcelain dish (E. & A. 2963, No. 00). Place in an air bath and dry for 3 hours at 100° C. Cool in desiccator and weigh. Burn off organic and volatile matter over a Bunsen flame, stirring occasionally. Cool in desiccator and weigh. Calculate percentages of organic and volatile matter and ash.

The nitrogen in the washed residue (previously determined for the alkaline permanganate activity) multiplied by 100 and divided by the organic and volatile percentage gives the "per cent. nitrogen in the organic and volatile matter."

Reference to the last column in the table shows that this figure varies in crude stock from 4.0 to 16.9, the relatively high figures corresponding to materials of recognized high grade and the low figures to those classed as inferior for plant food purposes. Thus dried blood shows 16.3 "per cent. of nitrogen in organic and volatile matter," fish 11.7, cottonseed-meal 9.4, medium tankage 9.2, while garbage tankage contains 5.1, peat 4.2, and mora meal 4.6 per cent.

Applying this procedure to commercial fertilizers licensed in Vermont from 1908 to 1911, inclusive, a range from 4 to 13.6 per cent. has been found, the low figures without exception corresponding to low organic nitrogen activity.

The organic and volatile matter in different mixtures of acid phosphate and muriate of potash has been found to vary from 3 to 3½ per cent., but as only a comparative figure is wanted, we have thus far made no correction when using the method on commercial fertilizers.

Fertilizer.	Per cent. nitrogen in the or- ganic and volatile matter.	Activity by alk. Perman- ganate method.	Fertilizer.	Per cent. nitrogen in the or- ganic and volatile matter.	Activity by alk. Perman- ganate method.
1	12.0	65 ¹	9	5.3	37
2	13.6	65 ¹	10	5.2	33.
3	11.8	73 ¹	11	9.0	69 ¹
4	4.0	39	12	9.1	68 ¹
5	5.1	49	1499	11.6	83 ¹
6	5.1	48	1546	9.6	73 ¹
7	5.5	48	1560	8.9	74 ¹
8	10.6	71 ¹	1573	6.7	52

As yet, we have found no sample of crude stock or fertilizer that does not show the desired relation-

ship between the percentage of "nitrogen in the organic and volatile matter" and activity of the water insoluble nitrogen, as measured by the alkaline permanganate method and vegetation tests. Thus, selecting at random from our results with commercial fertilizers collected during the past four years, the accompanying table indicates the general trend of results.

The point that the writer wishes to establish is that this determination of "nitrogen in the organic and volatile matter" will show whether the source of the water insoluble organic nitrogen is from materials rich in nitrogen or from those poor in this element.

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THE EFFECT OF THE "WET PROCESS" ON THE AVAILABILITY OF LOW GRADE NITROGENOUS MATERIALS.¹

By BURT L. HARTWELL AND F. R. PEMBER.

Received January 12, 1912.

It has been known for a long time that the nitrogen in such materials as roasted leather, garbage tankage and peat is of very low availability, and for that reason the fertilizer laws of certain states do not permit their use in fertilizers.

The claim has been made, however, by certain manufacturers that the so-called wet process of treating such materials so completely changes their physical and chemical nature that their availability is materially increased; and that, after having been subjected to the wet process, they should not then be considered in the same class as the original materials, nor discriminated against in the same way. Although these claims seemed reasonable, those charged with the inspection of fertilizers could hardly accept them without experimental proof.

Largely through the influence of a certain manufacturer of fertilizers, a fertilizer works was finally thrown open in 1910 to a committee, consisting of C. H. Jones, chairman, J. P. Street and B. L. Hartwell, which had been appointed by the Directors of the agricultural experiment stations of the New England States, New York and New Jersey to investigate the subject of the determination, by laboratory methods, of the availability of organic nitrogen.

This committee witnessed the mixing of about a hundred tons of hair tankage, garbage tankage, roasted leather, phosphate rock and sulfuric acid, by the wet process, took samples of all materials used in the mixture, and securely sealed the "den" containing the manufactured material. Two days later, the chairman of the committee, who was present at the breaking of the seals and opening of the den, took samples of the finished product. The identity of the nitrogenous material had been practically destroyed by the treatment. The maximum thermometer placed near the bottom of the den had registered 208° F.

The following determinations made by C. H. Jones show some of the changes which took place in the nitrogenous material during the process.

¹ Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

¹ Nitrogen readily available for plant use.

PER CENT. OF TOTAL NITROGEN PRESENT IN DIFFERENT FORMS.

	Before putting into the den.	After removing from the den.
In ammonium salts.....	6.5	14.3
In water soluble organic matter....	7.8	57.7
In water insoluble organic matter...	85.7	28.0

For vegetation experiments, the authors secured from the committee samples of the different nitrogenous materials which formed a part of the mixture, as well as of the final "base goods." Through the coöperation of Mr. Jones they were also supplied with similar low grade nitrogenous materials both in their unacidulated condition, and after they had been subjected individually to laboratory treatment with phosphate rock and sulfuric acid in a manner similar to that employed in the factory; in the case of each nitrogenous material, 500 grams of it were mixed with 750 grams of phosphate rock and 1250 grams of sulfuric acid.

Mr. Jones kindly furnished the following analyses of the material treated in the laboratory.

Per cent. of nitrogen in the material.

	Ammoniacal.	Water soluble organic.	Water insoluble organic.	Total.
Garbage tankage.....	0.02	0.23	2.61	2.86
Garbage tankage, acidulated..	0.06	0.20	0.27	0.53
Treated leather.....	0.03	0.65	4.74	5.42
Treated leather, acidulated...	0.04	0.78	0.16	0.98
Hair.....	0.28	0.60	10.77	11.65
Hair, acidulated.....	0.13	1.23	0.22	1.58

The nitrogen content of base goods made at the factory and of the identical materials which formed a part of the mixture, as finally used in the experiments, was as follows:

	Nitrogen. Per cent.
Hair tankage.....	6.28
Treated leather (roasted).....	6.49
Garbage tankage.....	2.87
Base goods, including the above.....	1.68
Water soluble nitrogen in base goods.....	1.28
Water insoluble nitrogen in base goods.....	0.40

The materials which were treated with phosphate rock and sulfuric acid in the laboratory ("acidulated"), and those mixed in the factory, were of about the same grade with the exception of the hair goods. The hair tankage used at the factory was a mixture of hair, wool, etc., which had undergone some decomposition, with the formation of ammonia, whereas that treated in the laboratory was clean, fine hair, on account of this difference, both grades were included in the pot experiment.

The vegetation experiments were conducted in eight-inch Wagner pots. Natural soil from two different localities was used. Optimum amounts of lime, potassium, and phosphorus were provided in hydrated lime, sulfate of potash, Thomas phosphate and acid phosphate, in order that the differences in growth might be attributable only to differences in the availability of the nitrogen. Unless stated otherwise the same amount of nitrogen for each crop (0.1 gram) was added per pot in the different materials.

The results are given in the accompanying table.

GRAMS OF AIR-DRY CROPS GROWN SUCCESSIVELY WITH THE SAME AMOUNT OF NITROGEN, UNLESS OTHERWISE STATED. ADDED PER POT FOR EACH CROP.

Source of nitrogen.	Grown in "Station" soil.			Grown in "Larkin" soil.		Average relative increase in yield (Blood = 80)
	Japanese millet.	Oats.	Buckwheat.	Oats.	Japanese millet.	
None (check).....	48.5	22.0	10.3	42.0	37.5	0
	50.0	23.5	9.3	48.5	35.5	
	49.5	24.0	8.0	44.0	35.5	
Hair tankage.....	53.0	30.5	14.5			
	49.5	32.0	11.3			59
Hair.....	48.5	28.0	11.0			
	49.5	30.0	11.5			33
Ditto, acidulated.....	55.5	31.0	12.5			
	52.0	31.0	11.0			64
Treated leather.....	51.0	25.5	12.5			
	50.5	24.0	10.5			23
Ditto, acidulated.....	56.0	33.0	16.5			
	56.0	29.0	10.0			80
Garbage tankage.....	48.0	22.5	10.5	48.0	40.0	
	48.0	24.5	9.5	46.0	41.5	13
Ditto, acidulated.....	49.0	22.0	8.5	50.5	34.0	
	48.5	21.5	10.0	54.0	34.5	8
Hair tankage, garbage tankage, and treated leather.....	48.0	29.5	11.0	54.0	43.0	
	47.0	29.5	10.3	56.0	44.0	49
Ditto, acidulated (base goods).....	52.5	30.5	17.0	54.0	52.0	
	50.0	31.5	12.5	57.0	49.0	84
Insoluble part of base goods.....	43.5	22.0		44.0	36.0	
	48.0	20.6		46.0	43.0	0
Dried blood.....	50.5	33.0	12.0 ¹	50.0	48.0	
	53.0	32.5	12.5	52.0	50.5	80
	52.0	30.0	21.0	54.5	49.0	
Ditto, with extra phosphorus.....	54.5	38.0 ²	26.5 ²	53.0	44.0	
	50.5	40.5 ²	26.0 ²	53.0	46.5	
Water soluble part of base goods.....	55.0	41.5 ²		53.0	51.0	
	58.7	40.0 ²		62.0	47.0	
Extra amt. blood.....	56.5	40.0	28.0	55.0	61.0	
	60.0	42.0	24.3	57.0	61.0	
Nitrate of soda.....	57.0	50.0 ²		61.0	49.0	
	56.5	46.5 ²		54.0	52.0	

In spite of the fact that an attempt was made to secure soils which were deficient in nitrogen, the first crop in the case of each soil proved to be nearly as large from the check pots, which received no nitrogen, as from the others. This is not an uncommon experience even with soils which have grown crops for some time without nitrogenous manures. It results from the fact that the application of lime, which proved necessary to maintain a soil reaction which was neutral to litmus paper and conducive to the utilization of organic nitrogen, led to the liberation of sufficient nitrogen to support a nearly maximum crop.

Although in the case of both soils, for the reason stated previously, distinct differences did not result from the different applications, it was decided nevertheless to include the results with those secured with the subsequent crops grown in the same soils after renewing the manurial applications including the nitrogenous materials.

The different nitrogenous substances, therefore, not only had an opportunity to exert their effect upon the crop immediately following their application,

¹ Omitted from the average.

² Received the same amount of nitrogen as was in the extra amt. of blood.

but also their after-effect upon one or two succeeding crops.

In the last column of the table is given the relative availability of the nitrogen in the different materials, arbitrarily considering 80 as the availability of the nitrogen of the dried blood (13.62 per cent. nitrogen), and deriving the availability of the nitrogen in the other materials from the increase in growth in each case over the appropriate check crops as compared with the increase caused by the dried blood. It is evident that only such of these values as are based upon results with the same number of crops should be strictly compared.

The comparisons which should be emphasized in this connection are those concerning the availability of the nitrogen in the materials before and after being "acidulated," or subjected to the wet process.

It may be seen that although the availability of the nitrogen is 33 in the unacidulated hair and 23 in the treated leather, the availabilities are increased to 64 and 80, respectively, in the same material after being subjected to the wet process in the laboratory. The nitrogen in the garbage tankage, however, had a very low availability both before and after treatment. When the identical hair tankage, garbage tankage and treated leather, which were used in the fertilizer factory for the manufacture of the base goods, were applied to the pots in the same proportions as used in the works, the availability of the nitrogen was 49, whereas that in the base goods made from the same materials was 84.

About 90 per cent. of the nitrogen in the various unacidulated materials was insoluble in water, and although a half of the total nitrogen in the garbage tankage was still insoluble after acidulation, only about a fifth of the nitrogen in the acidulated roasted leather and hair tankage remained insoluble.

That part of the nitrogen of the base goods which was rendered soluble by the wet process seems to have had an availability higher than that in blood, whereas the insoluble nitrogen was practically useless.

Vegetation experiments to determine the availability of the nitrogen in such material as base goods, containing large amounts of available phosphorus, have to be conducted with every possible precaution to prevent the results being influenced by the phosphorus. The details of the consideration given to this matter in the present instance would be out of place in this brief paper. The principle was followed of supplying phosphorus so liberally that more would be without influence on the crops. It may be seen by reference to the table that when an extra amount of phosphorus was furnished in addition to the application of the dried blood, which served as a standard, no increase of crops resulted. Nevertheless, it is best to be conservative in comparing the nitrogen availability of highly nitrogenous non-phosphatic materials, like hair, leather and blood, with the same materials when existing in a mixture with a nitrogen content of less than 2 per cent. and with a high content of phosphorus. Furthermore, when such comparatively small differences as exist in experiments of this kind between the weights of the crops from the check

and from the dried-blood pots are divided into 80 parts, it is evident that the "limit of error" is wide, and that certainly a difference of less than 10 in availability is of very little significance.

In view of these considerations, the claim is not made, therefore, that the nitrogen in acidulated leather and base goods is as valuable as that in dried blood. It is believed, however, that the experiments prove the efficiency of the wet process, when properly carried out, for materially increasing the availability of certain low-grade nitrogenous materials.

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NEUTRAL AMMONIUM CITRATE SOLUTION.¹

By A. J. PATTEN AND C. S. ROBINSON.

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Since the proposal of the ammonium citrate method for the determination of available phosphoric acid, much trouble has been experienced in preparing a strictly neutral solution of the reagent. The weakness of both the acid and the base renders the end point quite indistinct with ordinary indicators, and much time and patience are required on the part of the operator to obtain the desired results. Several modifications of the simple titration method have been proposed, but each has objections which prohibit its common acceptance by practical chemists. The importance which the method has assumed in agricultural work demands, however, that some convenient means be devised for preparing the necessary solution. Such a method has recently been proposed by Hall and Bell² and was later shown by Hall³ to be quite suitable for laboratory use. At the time these articles appeared, the authors of this paper were engaged in working out the same method, and the results are here offered, not with the hope of claiming the credit for originating the method, but simply as corroborative evidence in favor of its general adoption.

Of the several methods proposed as substitutes for the present official method, that recently suggested by Hand,⁴ using purified litmus solution or azolitmin, seems to be the most promising. In order to test it out and compare it with the official corallin method as well as to obtain some data as to the accuracy of the latter an acid solution of ammonium citrate was made up and neutralized by these two methods by each of four analysts working independently.

An acid citrate solution was chosen of which 50 cc. required 7.50 cc. of the dilute ammonia solution for neutralization as determined by the conductivity method to be described later. The dilute ammonium hydroxide solution (about 3 per cent.) was kept in a burette enclosed in opaque paper to prevent the reading being taken until the supposed neutral point had been reached. In this way each operation was made independently of the others. Great care was taken that no loss of ammonium hydroxide should occur

¹ Presented at the American Chemical Society Meeting at Washington, D. C., December, 1911.

² *Jour. Am. Chem. Soc.*, **33**, 711 (1911).

³ *THIS JOURNAL*, **3**, 559 (1911).

⁴ U. S. Dept. of Agric., Bur. of Chem., *Bull.* **132**, p. 11.