

other operations by disconnecting the apparatus. The drawing shows the table as it is used during the winter months, three steam tables being removed and in their place apparatus set up for steam distillation.

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## THE COMPOSITION OF HUMUS.

BY HARRY SNYDER.

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THE organic compounds of the soil to which the term humus is collectively applied, are a group about which but little is actually known. The humus compounds have not been extensively studied because of the difficulty of separating and obtaining them in a pure state. They do not form well-defined crystalline compounds, and they are all about equally soluble in various reagents. In fact, the analyst, when working with the humus compounds, is never sure whether he is working with a single compound or a mixture of several compounds.

The usual method employed in soil analysis for the determination of the humus compounds is the Grandeau or some modification of that method, which consists of first treating the soil with cold dilute hydrochloric acid to remove the lime, and then, after washing with distilled water, extracting the humus materials with a dilute ammonia solution. The humus extract is evaporated to dryness, dried, weighed, ignited, weighed again, and the loss of weight calculated as humus.

Inasmuch as the organic compounds of the soil may be derived from so many different sources, as any form of decayed animal or vegetable matter, it must necessarily follow that humus is very complex in composition. It seemed best, in this study of the composition of humus, to produce the humus from known materials, rather than to start with humus from unknown sources. Humus was prepared in the following way: A soil containing only a small known amount of organic material was used. About 200 grams of sugar were mixed with 3,000 grams of soil, placed in a tight box, and allowed to undergo humus formation, out of doors, for one year. Humus was produced in this way from a variety of materials, as cow manure, green clover, meat scraps, wheat flour, saw dust, oat straw, and sugar.

The humus materials produced from these various substances were obtained by extracting the soil, after treatment with dilute hydrochloric acid and distilled water, with a three per cent. potassium hydroxide solution. The alkaline humus extracts were neutralized with hydrochloric acid, which gave black and brown precipitates of humus materials, which were washed, dried, and prepared for analysis. The precipitated humus materials contained from five to twelve per cent. of ash, and had the following ultimate compositions, on an ash-free basis:

	HUMUS PRODUCED BY						
	Cow manure. Per cent.	Green clover. Per cent.	Meat scraps. Per cent.	Wheat flour. Per cent.	Oat straw. Per cent.	Sawdust. Per cent.	Sugar. Per cent.
Carbon.....	41.95	54.22	48.77	51.02	54.30	49.28	57.84
Hydrogen...	6.26	3.40	4.30	3.82	2.48	3.33	3.04
Nitrogen....	6.16	8.24	10.96	5.02	2.50	0.32	0.08
Oxygen.....	45.65	34.14	35.97	40.14	40.72	47.07	39.04
Total.....	100.00	100.00	100.00	100.00	100.00	100.00	100.00
	Highest. Per cent.			Lowest. Per cent.			Difference. Per cent.
Carbon.....	57.84 sugar.			41.95 cow manure.			15.89
Hydrogen ...	6.26 cow manure.			2.48 oat straw.			3.78
Nitrogen ....	10.96 meat scraps.			0.08 sugar.			10.88
Oxygen .....	47.07 sawdust.			34.14 green clover.			12.93

The differences in composition are noticeable. The humus produced by each material, as meat scraps, green clover, or sawdust, is different from the humus produced by every other material. There is not a general similarity in composition between the humus produced by any two of the materials. The humus produced by sugar may be taken as a type of a non-nitrogenous humus. The small amount of nitrogen present in the sugar humus has been derived from the nitrogen present in the soil. The humus from meat scraps may be taken as a type of humus produced from a nitrogenous material. The nitrogen content of the humus ranges from about one-tenth per cent. in sugar humus to nearly eleven per cent. in the meat scraps humus. The humus from materials as meat scraps and green clover must be exceedingly complex, because each material is composed of both nitrogenous and non-nitrogenous compounds, and each class of compounds is capable of being

split up into still other compounds, each one having a different action in humification processes. It is evident that any formulas applied to the compounds, as a whole, would, to say the least, fail to express the composition of humus.

Although the proximate composition of humus as yet, can not be given, or formulas assigned to these compounds, the nature of the humus as nitrogenous or non-nitrogenous can be determined.

There appears to have been no classification of the humus compounds proposed since the classification of Müllder, in 1840, as follows :

	Ulmic and ulmic acid. Per cent.	Humin and humic acid. Per cent.	Crenic acid. Per cent.	Approcrenic acid. Per cent.
Carbon.....	67.1	64.4	44.0	34.4
Hydrogen.....	4.2	4.3	5.5	3.5
Nitrogen.....	...	...	3.9	3.0
Oxygen.....	28.7	31.3	46.6	39.1
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

Corresponding to  $C_{40}H_{28}O_{12} + H_2O$ ;  $C_{21}H_{24}O_{12} + 3H_2O$ ;  
 $C_{12}H_{12}O_8$  (?);  $C_{24}H_{24}O_{12}$  (?)

None of the humus materials produced in these culture experiments have the same composition as given above. The sawdust and sugar humus approach in composition nearest to the humic and ulmic compounds. The differences are, however, great.

It would seem best, in the present state of knowledge, to make the divisions on the basis of nitrogen, as :

I. The non-nitrogenous humus group, as sugar humus.

II. The nitrogenous group, divided into three or four sub-groups, as (1) humus containing one to two per cent. nitrogen, as sawdust humus; (2) humus containing two to four per cent. nitrogen, as oat straw humus; (3) humus containing four to eight per cent. nitrogen, as cow manure and clover humus; and (4) humus containing over eight or nine per cent. nitrogen, as meat scrap humus.

Such a division would give an approximate idea as to the nature of the materials from which the humus has been derived, as well as an approximate idea of its agricultural value. As ordinarily used, the term humus is a very indefinite one so far

as conveying any idea as to its chemical composition or probable value.

*Formation of Humates.*—The analysis of the ash from the precipitated humus compounds shows the presence of potassium, calcium, iron, aluminum, phosphorus, sulphur, and other elements. There is every indication that these elements are in organic combination with the carbon, hydrogen, nitrogen, and oxygen of the humus. When the alkaline humus solution is neutralized, the ash elements are precipitated with the humus materials. The mineral matter combined with the humus is different in composition and solubility from ordinary soil. The average composition of the ash from eight samples of precipitated humus was found to be as follows:

	Percent.
Insoluble matter (HCl).....	61.97
Potash .....	7.50
Soda .....	8.13
Lime.....	0.09
Magnesia.....	0.36
Alumina .....	3.48
Ferric oxide.....	3.12
Phosphorus pentoxide.....	12.37
Sulphur trioxide .....	0.98
Carbon dioxide.....	1.64

Is the mineral matter, combined with humus, derived entirely from the mineral matter originally present in the humus-forming material, or is a part of it derived from the soil by the chemical action of the humus? That is, does the humus combine with the mineral matter of the soil to form compounds known as humates? In order to obtain data upon this question, initial and final weights of the soil and humus-forming materials used in the humus production experiments reported, were made, and the total grams of humic phosphoric acid and potash, in both the original soil and humus material, as well as the final product of the humus, were calculated. In many cases there were decided gains, showing that some of the mineral matter of the soil had entered into chemical combination with the humus-forming materials. In the following table the figures given for the original soil and humus are for the amounts present in the soil in humic forms plus the total amount of mineral matter in the substance used:

	Humic phos- phorus pentoxide. Grams.	Humic potash. Grams.
Cow manure humus.		
Original soil and manure.....	1.17	1.06
Final humus product .....	1.62	1.27
Green clover humus.		
Original soil and clover.....	3.21	5.26
Final humus product.....	3.74	4.93
Meat scraps humus.		
Original soil and meat scraps ...	1.07	0.25
Final humus product.....	1.18	0.36
Sawdust humus.		
Original soil and sawdust .....	0.85	0.67
Final humus product .....	0.78	0.70
Flour humus.		
Original soil and flour .....	0.60	0.32
Final humus product .....	0.71	0.48
Oat straw humus.		
Original soil and straw.....	1.02	2.42
Final humus product .....	1.03	2.41

There appears to be a great difference in the power which various materials possess of entering into chemical combination with the mineral matter of the soil to form humates. Some of the nitrogenous compounds seem to have a greater power of combining than the non-nitrogenous compounds. There is also a great difference in soils: some combine with the humus materials more readily than others.

The ultimate composition of the humus from different types of soil shows as wide a range as in the case of the humus prepared from the culture experiments. The nitrogen content of the humus ranges from one to ten per cent. The following examples show a range from six to ten. No. 1 is a sample made up of equal parts of eight rich prairie soils. No. 2 is a soil that has been under cultivation for a number of years. Nos. 3 and 4 are different types of soil. No. 3 has never been under cultivation, while No. 4 is a similar soil which has been cultivated for about forty years to small grains.

	No. 1. Per cent.	No. 2. Per cent.	No. 3. Per cent.	No. 4. Per cent.
Carbon.....	45.12	48.16	44.12	50.10
Hydrogen.....	3.67	5.40	6.00	4.80
Nitrogen.....	10.37	9.12	8.12	6.54
Oxygen.....	28.60	33.16	35.16	33.66
Ash.....	12.24	4.16	6.60	4.90

The humus from soils Nos. 1 and 2 would belong to the fourth class, while Nos. 3 and 4 would belong to the third class of nitrogenous humus compounds. For reasons given it would be impossible to assign, from these analyses, any formulas to the humus. The next best thing that can be done is to assign to the humus its probable agricultural value, which can best be done on the basis of the nitrogen content of the humus. This would involve simply a determination of the humus, and also a determination of the nitrogen content of the humus. The following working directions for these two determinations have been found to work well with ordinary soils.

*Determination of Humus.*—Weigh out either five or ten grams of soil into a 200 cc. wide mouthed glass-stoppered bottle. If the soil is poor in organic matter, fifteen or twenty grams should be taken. Add 100 cc. of a one per cent. solution of hydrochloric acid. If the soil contains more than one per cent. lime, then a two per cent. solution of hydrochloric acid may be used. Place the stopper in the bottle and shake vigorously. After allowing the acid to act on the soil for five or ten hours the solution is decanted into a filter, a fresh quantity of 100 cc. of acid is added, it is decanted, and the contents of the bottle are transferred to the funnel. The soil, in the funnel, is then washed with the dilute acid until no reaction for lime is obtained, and then with distilled water until the washings are only slightly turbid with silver nitrate. After receiving the above treatment the soil is transferred from the funnel to the stoppered bottle, using 150 cc. of a three per cent. solution of ammonia. The bottle containing the soil and ammonia solution is occasionally shaken, and after five or six hours the solution is decanted into a 500 cc. measuring flask. A fresh quantity of about 100 cc. of ammonia is added to the soil in the bottle, and after acting on the soil for three or four hours it is decanted and added to the first extract. After the third extraction, the extract usually becomes nearly colorless. After the fourth extraction the humus solution in the flask is made up to 500 cc. and allowed to settle. If the soil contains a large amount of fine clay it will be necessary to allow from two to ten hours, or longer, for the soil particles to settle. A 50 or 100 cc. portion of the filtered humus extract is evaporated to dryness in a tared platinum dish. After

drying in an air-bath at  $101^{\circ}$  or  $102^{\circ}$  (on account of the tenacity with which the humus retains water), the dish with the humus materials is weighed, then ignited, and weighed again. The loss of weight is calculated as humus. The humus extract may be either black or brown.

*Nitrogen Content of the Humus.*—Either five or ten grams of soil are first treated with dilute hydrochloric acid, in the same way as in the humus determination. If the soil contains only a small amount of organic material, fifteen or twenty grams should be taken for this determination. After treatment with acid the soil is extracted with a three per cent. solution of sodium hydroxide in the same way as for the ammonia extraction. Two hundred cc. of the filtered solution are evaporated nearly to dryness in a Kjeldahl distillation flask, after first making the solution acid with sulphuric acid. The nitrogen determination is then completed in the usual way.

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## THE ACTION OF CERTAIN BODIES ON THE DIGESTIVE FERMENTS.

BY FRANK D. SIMONS.

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VERY little attention seems to have been given to the study of the action of some of our common coloring matters, flavoring extracts, and preservatives on the digestive ferments. The object of my work, therefore, has been to test, from a physiological standpoint, the deportment of members of the above three classes of bodies towards digestion.

As far as my searches have extended, I have been able to find but very little literature bearing on this subject. Professor Chittenden, of the Sheffield Scientific School, has furnished many valuable contributions to our knowledge of digestion. He includes in a list of bodies antagonistic to the peptic ferment, potassium permanganate, borax, ammonia-alum, sodium salicylate, quinine, and the salts of nearly all of the alkaloids.

Dr. H. A. Weber<sup>1</sup> investigated the behavior of three coal-tar coloring matters (*viz.*, oroline yellow, saffoline, and magenta) towards digestion. Although these bodies have been included in the list of harmless colors, yet he found that each one, even

<sup>1</sup> This Journal, 18, 1092, 1896.