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SOME OF THE CHEMICAL AND
PHYSICAL PROPERTIES OF
SOIL HUMUS

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SOME OF THE CHEMICAL AND PHYSICAL PROPERTIES OF SOIL HUMUS

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The purpose of this discussion is twofold: first, to review the present status of knowledge concerning soil humus and its properties, and second, to set forth the results of certain investigations into those properties.

Of all the terms that have ever been used in agricultural literature, no term has been used so glibly and so effectively to cover a great mass of ignorance as has the term "humus." In order to be more definite the present discussion will be limited largely to the portion of the organic content of the soil, constituting the black, waxy coating of the soil grains. It must be recognized, however, that we have in our ordinary agricultural soils types of organic matter which are either entirely undecomposed, or have not reached that stage of decomposition called humus.

It is interesting to note the attempts that have been made to define or describe humus. Warington¹ says: "Humus is a mixture of many ill defined bodies; it may be roughly divided into humic acids and humin." Storer² says: "Little is known as yet as to the chemical composition of humus." Hilgard³ speaks of humus as a "complex mixture of dark-tinted substances resulting from the decay of vegetable substances."

¹Warington: Chemistry of the Farm, p.36.

²Storer: Agriculture, Vol.II, p.187.

³Hilgard:Soils, Chap.II, p.21.

A. D. Hall¹ voices the same opinion in stating, "the chemical composition of humus is indefinite; it is a variable mixture of several substances, themselves of very complex constitution."

Artificial humus bodies have been prepared from cellulose and other carbohydrates by boiling with acids or alkalis. The dark tinted amorphous bodies thus obtained, however, differ fundamentally from soil-humus in that they do not contain nitrogen, and are also lacking in the inorganic constituents uniformly found in soil humus; such as calcium, iron, magnesium, potash, and phosphorus. One investigator, Udransky², has succeeded in obtaining a nitrogenous humus body by boiling glucose and urea in hydrochloric acid. The humic bodies obtained by Udransky are not analogous to soil humus since their nitrogen was derived from the simple substance, urea, while the source and nature of humic nitrogen has been shown by Suzuki³ to be protein bodies.

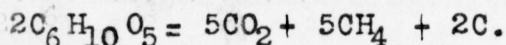
The scientist, whose name is invariably associated with a study of humus, is that of the Frenchman, Grandeau⁴. Grandeau early recognized that certain processes were at work in the soil converting a portion of the organic matter annually returned to the soil into the black, waxy substance

¹A.D.Hall: The Soil, Chap. II, p. 42.

²Udransky: Zeitschrift für physiol. Chemie, Bd.XII, p.42.

so familiar to all. This question, therefore, naturally arises: "What are, and what have been the agents producing humus?" A full discussion of this question would lead us into the whole wide realm of soil biology, and hence can only be briefly dwelt upon here.

Some soil bacteriologists would regard the process of humification as being pre-eminently bacteriological. Winogradsky's pupil, Omelianski¹ in his studies upon cellulose fermentation looks upon the common methane fermentation (caused by specific organisms) as very important in this process. He bases his conclusions upon the general formula:



Vorhees and Lipman² in their Review of Soil Bacteriology quote him as follows: "It is possible that a reaction of this sort forms the basis of the universal processes of humification - that is, the gradual transformation of organic substances into a mixture of brown and black substances with a high carbon content, such as is characteristic of fossil coals. But, whatever the mechanism of these transformations, the active participation of micro organisms in the latter cannot be denied." Hilgard³ denies to bacteria any participation in this process, asserting that the various higher

¹ Omelianski: Centralblatt für Bakteriologie, 2 abt., 8(1902) p.193; 11(1904) p.369; 12(1904) p.33; 15(1906)p.673.

² Vorhees & Lipman: A Review of Investigations in Soil Bacteriology, Bul.194, Office of Expt. Sta., p.21.

³ Hilgard: The Soil, Chap.VIII, p. 123.

fungi and moulds are the principal agents. Hilgard¹ bases his argument upon the discovery of a zone of mould growth constantly occurring around decaying roots and leaves. The only general conclusions that can be drawn from the evidence at hand is that humification is the process of decay and transformation of fresh organic material, brought about by both chemical and biological agents, or combinations of these forces.

Whatever the mechanism at work, the results of the process are well known, and remarkably constant, namely an elimination of the oxygen and hydrogen content of the original organic substance and a concentration of the carbon and nitrogen content; and probably a concentration of the ash content. The nitrogen and ash content of humus are the elements of importance from an agricultural standpoint.

Carbon constitutes approximately sixty per cent of the organic content of the soil. Although present in such comparatively large quantities in the soil, the nature of this carbon content is little understood. The consensus of opinion of the early writers was that the carbon existed in the soil as an integral part of such substances as humic and ulmic acids, crenic and apocrenic acids; humin and ulmin.

Mulder² in his "Chemie der Ackerkrume" thus describes the

¹Hilgard: The Soil, Chap. IX, p. 157.

²Mulder: Chemie der Ackerkrume, Band II, p. 256.

organic matter of the soil. Attempts at analysis and isolation of such bodies have lead modern investigators to the conclusion that there is no good reason for assuming the existence of these indefinite organic compounds, with the possible exception of humic acid.

Since humus is the product of the decomposition of vegetable matter, it was formerly supposed that a large part of the humic nitrogen existed as ammoniacal and amino-nitrogen, instead of protein nitrogen. The classical researches of Shigehiro Suzuki¹ of Japan have disproved this, and have established the fact that humic nitrogen is principally protein in character, and that amino acids, as such, exist in humus as mere traces. Suzuki² demonstrated the existence of protein decomposition products by the application of E. Fischer's method for the separation of the amino acids. Suzuki's work must be criticised, however, on the ground that his principal work was done on a humic acid "whose origin and method of preparation were unknown."³ From 500 grams of "humic acid", probably originating from a peat soil, Suzuki⁴ obtained by hydrolytic cleavage with concentrated hydrochloric acid the following decomposition products of proteids:

¹S. Suzuki: Studies in Humus Formation III, Bul. Of College of Agriculture, Tokyo Imperial University, Japan, Vol.VII, No. 4, p.528.
²Ibid: pp. 511-529.
³Ibid: p. 516.
⁴Ibid: p. 529.

Alanin	"2.39	grams.
Leucin	2.16	"
Alanin and Aminovalerianic acid	0.11	"
Aminovalerianic acid	0.57	"
(copper salt of active	0.67	"
Prolin(" " " inactive	0.50	"
Aspartic acid	0.06	"
Impure aspartic acid	2.16	"
Glutamic acid	present	
Tyrosin	trace	
Histidin	trace	
Ammonia	1.90	
Copper salts of unknown acids	30.30	

The principal inorganic elements of the soil humus are calcium, magnesium, potassium, iron, and phosphorus. The potassium and phosphorus content of humus are of the most interest from an agricultural point of view. Potassium and phosphorus may possibly occupy either of two positions in that organic body, humus. Potassium may be present as a basic constituent and phosphoric acid as an acid constituent of a complex organic compound, or both may occupy a position similar to that of potassium in ordinary potassium alcoholate. The nature and properties of potassium-humic compounds, and phospho-humic compounds will very largely depend

upon their organic structure. Berthelot¹ claims to have produced a potassium humus compound which, although subjected to repeated washings, still retained 3.7 to 6.2 per cent of insoluble potash.

J Dumont², who prepared phospho-humic compounds by precipitating potassium and ammonium humates in the presence of phosphates, claims that similar compounds are formed in the soil.

The amount of phosphorus in combination with the organic matter extracted from the soil by ammonia is comparatively small. G.S.Fraps³ of the Texas Experiment Station in a study of the ammonia soluble phosphoric acid of the soil found only one-third of the ammonia soluble phosphoric acid in the organic precipitate as obtained in the usual Grandeau method for the study of humus. He⁴ further found that this portion of the phosphoric acid was non-diffusible and therefore concludes that it is in organic combination.

The agricultural value of the ash constituents of the humus is a disputed question. Snyder's⁵ experiments with precipitated humic acid indicate that they are of considerable importance. An extensive study of the phospho-humic compounds

¹M. Berthelot: On the insoluble alkaline compounds formed by artificial humus compounds of organic origin - Ann. Chem. et Phys. 8 ser. 8 (1906), May, pp. 45-51, cited from U.S. Expt. Rec.

²J. Dumont: The phospho-humic compounds of the soil - compt. Rend. Acad. Sci. 143, 1906, No. 3, pp. 186-189. Abstract in Jour. of Chem. Soc. (London) 90, 1906, No. 527, II, p. 626.

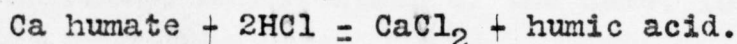
³G.S. Fraps: The Ammonia Soluble Phosphoric Acid of the Soil, mReprint from Am. Chem. Jour., Vol 39, No. 5, May, 1908, p. 586.

⁴Ibid: p. 586.

⁵Snyder: Humus as a Factor of Soil Fertility, Ann. Rpt. of Agr. Expt. Sta., for 1895, Univ. of Minn., pp. 12-31.

will undoubtedly furnish much of value to the student of soil problems.

Having set forth the importance of the constituents of humus, methods for its estimation will now be considered. Grandeau¹ recognized that the old method of estimating the total carbon content of a soil was not a true index of the humic content of the soil, since many soils contain large amounts of unhumified material. Furthermore, it was found essential for the study of humus that some means be found whereby it could be studied more or less intact. Grandeau, therefore devised the following method for the separation of humus from the soil: A weighed quantity of soil was first washed with two per cent hydrochloric acid until no further test for calcium was obtained in the wash water. The soil was then washed free from acid, and finally subjected to extraction with ammonia, fresh portions of ammonia being added to the soil until the filtrate obtained was no longer colored. The treatment with acid presumes the presence in the soil of calcium humate; thus:-



The humic acid thus set free reacts with the ammonia to form the soluble ammonia humate. The black extract thus obtained was evaporated to dryness to expel water and am-

¹L. Grandeau: Cited from Huston and McBride - A Modification of Grandeau's Method for the Determination of Humus, Indiana Expt. Sta., Bul. 46, Vol. IV, p. 69.

monia, the dry, shiny, waxy residue constituting Grandeau's "matière noire." This method has proved cumbersome; hence has been modified, but is still widely used in its various modifications. The principal objections to the method are the long time of operation, the use of varying strengths of ammonia, the placing of the soil in an open funnel, and the contamination of the black matter with clay. Huston and McBride¹ of Purdue University adopted the modification of Grandeau's method which follows: After the usual acid treatment and subsequent washing the soil is transferred to a 500 cc. stoppered cylinder with 500 cc. of ammonia, the cylinder being shaken at regular intervals for twenty-four hours and then allowed to settle for twelve hours. They studied the effect of different strengths of ammonia, and of different times of digestion upon the percentage of humus as obtained by this method and by Grandeau's method.

The data which they accumulated is so striking that it is given below:-

Comparison of Grandeau's Original Method, and Huston and McBride's Modification of the Same, for the Estimation of Humus.²

¹Huston and McBride: A Modification of Grandeau's Method for the Determination of Humus, Purdue University, Agr.

² Expt. Sta., Bul. No.46, Vol.IV of Rep'ts, pp.68-79.

Ibid: pp.68-79.

TABLE I.

Soil extracted with two per cent hydrochloric acid -
five grams of soil used.

	2% Ammonia		4% Ammonia		7.3% Ammonia	
	Gran- deau	Huston & McBride	Gran- deau	Huston & McBride	Gran- deau	Huston & McBride
Unproductive Peat Soil	9.61	15.74	15.03	20.72	19.81	21.80
Clay Loam	1.81	4.28	2.44	4.27	2.14	4.25

Soil extracted with five per cent hydrochloric acid -
two and one-half grams of soil used.

Productive Peat	15.78	20.87	19.02	23.24	20.05	30.53
Dark Clay Loam	2.45	4.71	3.07	4.54	2.70	7.06
Clay	.84	2.05	1/04	1.84	1.36	3.24

The following conclusions may be drawn from Huston and McBride's tables:

1. That the original Grandeau method is very unsatisfactory.
2. That the modified method is applicable to soils not too high in organic matter.
3. That the use of either ammonia or any caustic alkali is an inadequate means of estimating the humus in soils having a high organic content, such as peat, probably because these caustic alkalies themselves act as humifying agents.

The writer performed an experiment to ascertain whether the amount of humus was a straight line function of the strengths of ammonia used. Four samples of twenty-five grams each of air dry virgin clay loam soil were shaken with 400 cc. of one per cent hydrochloric acid for one hour in a mechanical shaker. The soils were then rinsed out into Gooch crucibles and washed free from acid. These four samples were treated respectively with 500 cc. of four per cent, two per cent, one per cent, and five-tenths per cent ammonia for twenty-four hours (shaken at regular intervals) and allowed to stand twelve hours. The black extract thus obtained was decanted through a filter paper and finally filtered through a Pasteur filter to remove the clay. In order to make the four samples more comparable, the filtrate thus obtained was in each case made up to 500 cc. and the humus

determined by evaporating to dryness 100 cc. portions of the respective solutions. The results obtained are tabulated below:-

TABLE II.
Effect of Strength of Ammonia.

Per cent ammonia.	Weight humus.	Per cent humus.
4	.3095	1.23
2	.3400	1.36
1	.2445	0.978
.5	.2525	1.010

This data indicates that in this particular soil the weight of the humic extract was not a straight line function of the strength of ammonia used. The filtration of the humic extract through the porcelain filter is open to the objection that the filter retains considerable slimy organic matter.

Other methods that are used for the estimation of humus are similar to the Grandeau method, excepting that they substitute sodium hydrate or potassium hydrate for ammonia.

Aschman¹ and Faber extract the soil with five per cent sodium hydrate, and finally determine the carbon in the humic extract by oxidation with an excess of potassium permanganate, the excess of potassium permanganate being titrated back with oxalic acid.

¹Aschman & Faber: On the Estimation of Humus, Chem.Ztg. 23 1899, no.7, p.61.

Peter and Averitt¹ of Kentucky Experiment Station claim that the results obtained by the official method for humus are too high owing to contamination with clay and ferruginous material. They, therefore, subtract ten per cent of the weight of the residue after burning the humus. No method has yet been devised that furnishes a complete separation of the humic bodies from the soil.

Properties of the Ammonia Extract.

From the ammonia extract as usually prepared the mineral acids precipitate a flocculent brownish-black substance, known as humic acid. The filtrate from this acid precipitation is clear but colored, indicating the presence of organic matter. According to Wollny² and as confirmed by others these humic acids are somewhat soluble in cold water, quite soluble in boiling water, but are insoluble in water acidulated with the mineral acids. These humic acids form compounds with ammonia, potassium hydrate, and sodium hydrate that are soluble in water. They combine with calcium, magnesium, iron, and manganese to form humates.

C. G. Eggertz³ found these humic acids to be almost

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Peter and Averitt: Kentucky Agr. Expt. Sta., Bul. No. 126, pp. 122-126.

²Wollny: Die Zersetzung der Organischen Stoffe, pp. 214-223.

³C. G. Eggertz: Studien und Untersuchungen über die Humuskörper der Acker und Moorerde: Bredemann's Centralblatt für Agrikulturchemie, pp. 75-80.

entirely soluble in ammonium carbonate, ammonium oxalate, ammonium phosphate, potassium carbonate, and sodium carbonate, but insoluble in ammonium chloride, ammonium nitrate, ammonium sulphate, and potassium phosphate. He further found that in ammoniacal chloride of lime the humic acids form a precipitate which is insoluble in water and the caustic alkalies, but dissolves slightly in ammonium chloride, ammonium nitrate, and ammonium sulphate. This calcium precipitate dissolves in ammonium oxalate, ammonium carbonate, sodium carbonate, potassium carbonate, and ammonium phosphate.

Detmer¹ has found that humic acid dissolves less readily in solution of potassium nitrate, sodium chloride, and potassium chloride than in water. According to his determinations, one part of humic acid is soluble in 8,333 parts of water at 43° Fahrenheit, and in 3,571 parts at 65° Fahrenheit.

Grandeau² subjected the ammoniacal extract to dialysis and found that in thirty-six hours, eighty-six per cent of the ash content of the extract had dialyzed through the membrane, but that no colored matters passed through, indicating the colloidal nature of the humus. This experiment has led some to the conclusion that plants can obtain the inorganic constituents of the soil humus in a very similar

¹Detmer: Cited from Storer's Agriculture, Vol.II, p.215.

²Grandeau: Cited from Storer's Agriculture, Vol.II, p.201.

manner.

In the course of this study certain properties of the ammoniacal extract were observed, the extract used being a composite sample from several soils. The precipitate obtained by adding mineral acids was gelatinous, and either ran through the filter paper and asbestos, or clogged the filter so that filtration was extremely slow. Because of this difficulty in filtering and washing the precipitate, it was found necessary to precipitate the ammoniacal extract in centrifuge tubes and then whirl the tubes at a speed of about 1,400 revolutions per minute for ten to twenty minutes. The humic acid was compacted in the bottom of the centrifuge tube by this operation so that the clear supernatant liquid was easily decanted through a Gooch filter. Washing was accomplished by whirling the humic acid several times with acidulated water. Complete neutralization of the ammonia extract, without an excess of acid, gave a clearer filtrate than when an excess of acid was used. Neutralization with hydrochloric acid gave clearer filtrate than when nitric acid was used. The solubility of the humic acid in pure water is so great that it is necessary to maintain an acid reaction in the wash water used. The humic acid thus obtained has the power of darkening filter paper to a very marked degree, so much so that filter paper should not be used in dealing with the substance.

Ten cubic centimeter portions of an ammoniacal filtrate were evaporated to dryness and treated with various organic solvents to ascertain what effect such solvents might have. Benzene, ethyl alcohol, ethyl acetate, amyl alcohol, and amylene were tried, but none had any solvent action.

Effect of Organic Solvents upon the Organic
Matter of the Soils.

Recognizing that the usual methods for estimation and separation of humus bodies involve the use of rather strong reagents, a study was made of the effect of certain organic solvents upon the soil directly.

This investigation aimed to select solvents that would have practically no effect upon the inorganic constituents of the soil.

The soil selected for study was a virgin soil corresponding to Plot 9 of the Soils Department Grounds. This soil is comparatively low in organic matter, containing 3.24 per cent according to the chromic acid combustion method. The sample was air dried and then passed through a twenty-mesh sieve.

Experiment 1.- Twenty grams of this air dry soil were placed in a digestion flask fitted with ground glass reflux condenser, seventy-five cc. of benzene added, and the whole digested for one hour on the water bath. The soil mass was then filtered off, and the benzene filtrate

evaporated to dryness. Only a trace of resinous material was obtained. Since resins are amorphous bodies, one may very properly suppose that they constitute a portion of the amorphous humus bodies contained in the soil. According to Holleman,¹ resins are often found as the result of secondary reactions in the decomposition of organic compounds.

Experiment 2.- Ammonium alcoholate was prepared by saturating absolute alcohol with dry ammonia gas. Twenty grams of oven dry soil were shaken with 100 cc. of this solution several times during a period of twenty-four hours. The soil mass was then filtered off, and the filtrate evaporated to dryness. There was absolutely no residue obtained.

Experiment 3.- A continuous extraction apparatus was set up, using the glass stoppered, reflux condenser flasks, and a Schleicher and Schüll paper capsule. Two grams of soil were placed in this capsule, and subjected to continuous extraction for three hours each, with the following solvents, in the order mentioned: ether, acetone, ethyl acetate, amyl alcohol, and pyridine.

The dry weight of residues thus obtained are tabulated below:-

50 cc. Ether0055	grams.
50 cc. Acetone0037	"
50 cc. Ethyl Acetate0022	"
25 cc. Amyl Alcohol0041	"
50 cc. Pyridine (six hours extraction)	.0049	"
	<u>.0204</u>	

¹Holleman: Walker Text-book of Organic Chemistry, p.69.

$.0204 \div 2 = .0102$ grams, or one per cent of the weight of the soil.

Since the soil contains a little over three per cent of organic matter (chromic acid method), it may be assumed that these organic solvents have extracted about one-third of the organic matter of this particular soil.

Experiment 4.- Two grams of soil were treated with three grams diphenylamine and 25 cc of ninety-five per cent alcohol to ascertain whether or not such an organic base would extract any dark colored bodies, such as ammonia extracts. There was no evidence of any extraction by this method.

The experiments with organic solvents have lead to the following general conclusions:-

1. That the humic bodies in the soil are entirely too inert to be attacked by substances that are solvents only.
2. That much of the material extracted by the organic solvents may have been extracted from unhumified material.

Comparison of Sodium Hydrate and Ammonia
as Solvents for Soil Humus.

Since sodium hydrate is considerably used in the extraction of humus from the soil, a series of experiments were planned in which the amounts of humic acid extracted

by ammonia and sodium hydrate, with and without previous acid treatment, were to be studied. Owing to the lack of time, some of the experiments planned were not completed. The method of extraction was as follows: Twenty-five grams of air dry soil were placed in a flask, fitted with a reflux condenser. Two hundred fifty cc. of sodium hydrate of the desired strength were added to the soil. The whole mass was then digested for three hours at the temperature of the boiling water bath. The flame was then removed and the supernatant liquid in the flask allowed to settle twelve hours, whereupon it was filtered through a paper filter in the case of two per cent sodium hydrate, and through a dried Gooch filter in the case of four per cent sodium hydrate. Since sodium hydrate does not exert a defloculating effect upon the clay, an extract was obtained, which was free from clay. Twenty-five cc. of this extract was placed in a centrifuge tube, diluted with twenty cc. of water, neutralized with hydrochloric acid, and the precipitate whirled down and washed as heretofore described. These precipitates were dried at 110° and then weighed, and their weight compared with the weight of the humic acid obtained from the ammoniacal extract.

The method used for obtaining the four per cent ammoniacal extract was the same as detailed heretofore, with the exception that the extract was not made up to volume

after filtration through the Pasteur filter. The soil was given the usual one per cent acid treatment previous to extraction with ammonia. The humic acid was separated by precipitation with hydrochloric acid. The results obtained are expressed below:-

Average weight of humic acid from four per cent sodium hydrate extract without acid treatment0204 grams.
Average weight of humic acid from four per cent sodium hydrate extract with one per cent acid treatment0219 "
Average weight of humic acid from four per cent ammonia extract with one per cent acid treatment0086 "
Average weight of humic acid from two per cent sodium hydrate with one per cent acid treatment0209 "

These results indicate that in this soil, a clay loam containing 3.24 per cent organic matter, over twice as much organic matter is extracted by two and four per cent sodium hydrate as is extracted by four per cent ammonia.

Charles Rimbach,¹ of the Agricultural Experiment Station of the University of California has obtained the

¹Rimbach: Investigations on the Determination and composition of Humus, and its Nitrification, Rpt. Agr. Expt. Sta., Univ. of California, 1898-1901, Part 1, pp. 43-48.

following data relative to the comparative extractive power of sodium hydrate and ammonia:-

		Wt. of humic acid precipitated by hydrochloric acid	Organic matter in the humic acid.
Peat Soil.	Ammonia extract, 200 cc.	0.1127	0.1120
	Sodium hydrate extract, 200 cc.	0.1495	0.1490
Adobe Soil.	Ammonia extract, 300 cc.	0.0299	0.0233
	Sodium hydrate extract, 300 cc.	0.0103	0.0077

The peat soil contained 19.12 per cent of humus, the adobe soil 1.20 per cent humus. It will be noticed that the sodium hydrate extracts more organic matter from the peat than does the ammonia, but that the reverse holds true in case of the adobe soil. Other experiments by Rimbach demonstrate very forcibly that more nitrogen is extracted from the soil by sodium hydrate than by ammonia. He considers that the question whether or not ammonia or sodium hydrate is the best solvent to be used in the study of humus, is an unsolved problem.

It must be borne in mind that sodium hydrate itself acts as a humifying agent. This is clearly shown by a microscopical examination of the soil residues after treat-

ment with the respective alkalies. The undecomposed sticks, roots, and portions of leaves in the soil are more attacked by sodium hydrate than by ammonia. It was further found that if a soil was treated with one per cent hydrochloric acid before extraction with sodium hydrate, that the soil grains were left much cleaner than where the soil was not given the previous acid treatment.

In the study of humus the problem of the proper solvent is probably the hardest one confronting the soil chemist. In this study many pertinent questions have arisen whose ultimate solution will probably aid in the study of the humus problem. For that reason it has seemed best to conclude this discussion with a presentation of the following questions:-

1. What is the quantitative relation of the organic content of the acid filtrate to the organic content of the black precipitate in the acid precipitation of the ammoniacal soil extract?
2. Does the filtrate and the flocculent precipitate contain the same kind of organic matter?
3. What is the ratio of the ash content of the filtrate to the ash content of the precipitate?
4. Is the ash of the unhumified material in the soil of more value to agricultural plants than that represented by humic ash?

5. Does extraction by sodium hydrate with or without previous acid treatment or by ammonia with previous acid treatment, give the best results from an agricultural point of view?

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