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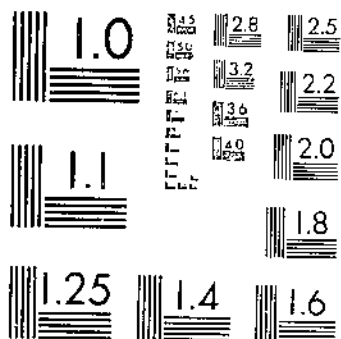
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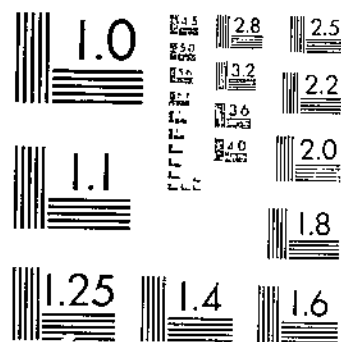
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CHARACTER AND BEHAVIOR OF ORGANIC SOIL COLLOIDS
ANDERSON, M. S.; BYERS, H. G.

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UNITED STATES DEPARTMENT OF AGRICULTURE
WASHINGTON, D.C.

CHARACTER AND BEHAVIOR OF ORGANIC
SOIL COLLOIDS

BY M. S. ANDERSON, *chemist*, and HORACE G. BYERS, *principal chemist*, Division of Soil Chemistry and Physics, Soil Investigations, Bureau of Chemistry and Soils

CONTENTS

	Page		Page
Introduction.....	1	Properties of organic colloids in mixtures—	
Character of organic colloids from various		Continued.	
soil-making materials.....	2	The role of organic colloids in soil-profile	
Behavior of organic colloids.....	4	formation.....	19
Relation of soil-making organic residues		Amphoterie character of soil organic matter..	19
to soil colloids.....	8	Acid treatment of organic soil colloids.....	20
Properties of organic colloids in mixtures....	8	Fractionation of soil organic matter.....	22
Water-vapor absorption by colloid mix-		Chemical character of extracted mate-	
tures.....	10	rials.....	23
Ammonia absorption by colloid mixtures.....	11	Fundamental variations in soil organic	
Hydrated oxides and acid organic col-		matter.....	29
loids.....	13	Summary.....	29
Water-vapor absorption by synthetic gel		Literature cited.....	30
mixtures with organic colloids.....	17		
Reactions of organic colloids with ferrous			
hydroxide.....	17		

INTRODUCTION

The importance of organic matter in the soil has been recognized since the earliest soil investigations, and an enormous literature has accumulated. At different periods emphasis has been placed upon different phases of the subject. A few years ago the isolation and identification of organic compounds occurring in the soil was extensively studied. Schreiner and Shorey (34),¹ of the Bureau of Chemistry and Soils, made important contributions along this line. In all those studies the organic material was extracted from the soil by alkalis, which involves the probability of drastic alteration of its properties, and also leaves a material fraction of it in the soil residue, or it was extracted by the use of solvents selected for the express purpose of obtaining fractions of special types of organic matter.

Very little special study has been made of the properties of organic colloids as such. Information concerning the organic portion of the soil colloid is, therefore, either indirect or was obtained by the study of materials more or less drastically altered by treatment. This situation is doubtless owing to the fact that the soil organic and inorganic colloidal materials occur in very intimate relation to one another. When soils are subjected to treatment designed to disperse and isolate the colloids, both the organic and the inorganic

¹Italic numbers in parentheses refer to literature cited, p. 30.

portions disperse together. To the present time no adequate treatment has been devised which is effective in bringing about a satisfactory separation, whether based upon relative specific gravity or dispersibility of the material.

The findings presented in parts of this bulletin resulted in part from the belief of the writers that some progress in the study of organic soil colloids might be made if colloids of the type of those occurring in the soil could be secured and their properties determined, and then, by adding them to inorganic colloids of known properties, the mutual effects could be ascertained. As the work progressed portions of organic matter from different soils were separated in various ways and these fractions added to the group studied.²

No attempt is being made at this time specifically to define organic soil colloids. For the purposes of this bulletin, however, the term colloid is used to describe material which may be dispersed and separated by the use of the supercentrifuge in the same manner as the total colloidal material (14). In addition to this there are included materials rendered more or less soluble by different reagents and subsequently coagulated.

Interest in the study of organic soil colloids has arisen from various viewpoints. Important among these are the argillohumic complexes formed by Aarnio (1) by precipitating iron and aluminum salts with humic material; isoelectric precipitates recently studied by Mattson (20, 21) in which iron and aluminum salts were precipitated by humic acid; the argillohumic complexes prepared by Demolon and Barbier (11) by coagulating rotted straw with clay at varying pH values, and the various studies by Waksman and associates (36, 37).

CHARACTER OF ORGANIC COLLOIDS FROM VARIOUS SOIL-MAKING MATERIALS

The desired colloids were secured from various sources. Wheat straw, well rotted under natural conditions and never in contact with soil during the process of decomposition, was secured from Pennsylvania. A similar sample of barley straw and one of clover hay were obtained from Iowa. A sample of deep leaf mold, mainly birch, was secured from New Hampshire, and a rotted oak log from Virginia. N. R. Smith, of the Division of Soil Microbiology, prepared a considerable quantity of a common soil organism, *Pseudomonas fluorescens*, and Charles Thom, of the same division, kindly prepared a quantity of a common soil fungus, *Alternaria* sp. Both of these organisms were grown in media containing no colloidal material, and no water insoluble salts were added. In addition work was done with material from a Leon soil hardpan of Florida and two peat samples from Oregon, and with extracts from soils containing considerable organic matter, the fractions of which were probably considerably altered in properties by the extraction.

The colloids were all extracted in the usual manner employed in this Bureau: dispersion in water and centrifuging. The colloids were separated from the suspensions by Pasteur-Chamberland filters as a viscous mass and used in this condition or air-dried, according to the requirements of the experiments.

² Some of the data given in the first part of this bulletin were presented at the twelfth annual meeting of the American Soil Survey Association, November 1931, and a summary of this report was printed in the proceedings of that meeting.

The samples of bacteria and of fungus were prepared differently from the others, since they did not consist of material of colloidal size. The water cultures of bacteria were passed through a small high-speed centrifuge at a very slow rate of flow. The small amount of solid material passing through was discarded while the residue in the bowl was transferred to an electro-dialyzer and freed from diffusible ions. The fungus residue was thoroughly washed by decantation and dispersed as completely as possible with a Bouyoucos agitator. The suspension was then electro-dialyzed.

It is well known that the pH values of electro-dialyzed inorganic soil colloids vary with the concentration of solid material, the clear saturated solutions of these slightly soluble acids being of much lower hydrogen-ion concentration than the suspensions containing the solid material. The pH values of electro-dialyzed organic colloids were obtained with a bubbling hydrogen electrode, using a viscous water suspension, that is, about 1 part of colloid to 3 parts of water. Where clear supernatant solutions were obtainable, they were determined also. The results are given in table 1. Included in this table also are the ash contents of the electro-dialyzed colloids.

TABLE 1.—Hydrogen-ion concentration and ash content of electro-dialyzed organic colloids

Source of colloid	Viscous material	Clear solution	Ash	Source of colloid	Viscous material	Clear solution	Ash
	pH	pH	Percent		pH	pH	Percent
Leaf mold.....	3.2	6.2	3.0	<i>Alternaria</i> sp.....	3.2		2.8
Clover hay.....	2.7	5.1	14.3	Leon soil hardpan.....	3.3	5.2	35.9
Barley straw.....	2.7	4.5	18.1	Peat.....	3.1	4.7	42.0
Wheat straw.....	3.2	4.4	11.6	Becket soil extract 1.....	2.5	3.0	
<i>Pseudomonas fluorescens</i>	3.7	4.0	.6	Marshall soil extract 1.....	2.3		16.4

¹ These soils were treated with 5 percent NH_4OH , the extract filtered, precipitated with HCl , again filtered, and the precipitate electro-dialyzed.

The colloids obtained from materials not in contact with soil had ash contents ranging from 3.0 percent for leaf mold to 18.1 percent for the barley straw. The lowest ash content was shown by the bacterial residue. The ash contents undoubtedly affect the results of this study but at least they are not soil inorganic colloid. It is recognized, of course, that ash constituents are present in plant materials to the extent of several percent. In certain cases, particularly the straws and hay, the inorganic material apparently tends to concentrate in the more readily dispersible material. The colloid of the Leon sand, on the other hand, contained much more organic matter than the soil, which consists essentially of quartz sand cemented by organic material.

The hydrogen-ion concentration of the electro-dialyzed materials varied from pH 2.3 for the Marshall soil extract to 3.7 for the bacteria. The acidity of these colloids was, therefore, of the same order as that of the electro-dialyzed soil colloids recently reported by Anderson and Byers (4). Most of the clear solutions were more acid than those from inorganic soil colloids. This is taken as an indication that the acids of organic soil colloids are more soluble than the inorganic ones.

The organic colloids were subjected to analytical examination essentially as described by Feustel and Byers (13) in their study of peat profiles. Analytical data are given in table 2.

TABLE 2.—*Proximate chemical composition of colloids from various electrodialed materials*

Sample no.	Kind of colloid	Ether extract	Alcohol extract	Hot-water extract	Hemicellulose	Cellulose	Lignin
		Percent	Percent	Percent	Percent	Percent	Percent
5052	Wheat straw	0.44	2.73	12.27	3.24	0.99	39.8
5291	Barley straw	.30	1.64	7.32	1.73	1.03	61.2
5292	Clover hay	.30	6.33	5.83	3.43	.66	41.6
5784	Leaf mold	.21	6.41	1.80	6.09	2.58	52.2
5804	Leon soil hardpan	.61	.84	2.84	1.57	(1)	18.8
5873	<i>Pseudomonas fluorescens</i>	4.63	2.56	8.46	(1)	(1)	14.6
6931	<i>Alternaria</i> sp.	.64	2.98	6.29	9.32	5.19	29.0
7023	Peat	1.01	2.13	1.57	3.93	(1)	27.8

(1) Trace.

The presence of ether, alcohol, and water-soluble components is shown, and the two latter particularly are relatively high, the water-soluble material ranging from 1.57 percent for the peat colloid to 12.27 percent for that from wheat straw. Both cellulose and hemicellulose are present in significant amounts in most of the colloids, but are absent in the material of bacterial origin. The largest single component is the ligno-humic complex which ranges from 14.5 percent in the bacterial residues to 52.2 percent in the leaf mold. There are present in all the colloids varying quantities of nitrogenous material which was not determined. This may be assumed to be particularly large in the bacterial residue. There were present also significant quantities of material of a chitinous character.

BEHAVIOR OF ORGANIC COLLOIDS

Various other properties of the organic colloids were determined. Some of these determinations were made on the freshly dispersed and concentrated material and others on the materials after electrodia-lysis. One of the important properties of both organic and inorganic soil colloids is their capacity to neutralize or absorb bases. In the case of inorganic soil colloids, varying base-holding values may be obtained, depending upon the conditions of the experiment. In the present investigation a comparison is made of this behavior by two different methods, electrometric titration with sodium hydroxide and determination of the ammonium-absorption capacity. Three essentially inorganic soil colloids were also treated in the same manner. In each case the colloids were electrodialed as a preliminary treatment.

The colloidal materials, without previous drying, were transferred to a vessel for electrometric titration and sodium-hydroxide solution added slowly over a period of 48 hours, care being taken to prevent pH values from rising higher than 7.5 at any time. Approximate equilibrium was then obtained at pH 7.0 ± 0.2 . The values obtained for several colloids are given in table 3. In this table also are given the quantities of ammonia taken up by the colloids from 0.5 normal ammonium hydroxide and held after drying on a steam bath. The

ammonia present was determined by distillation with magnesium oxide.

TABLE 3.—Comparison of NaOH required to neutralize electrolyzed colloids and their ammonia-holding capacity

Source of colloid	NaOH required to neutralize 1 gram of colloid	NH ₃ held by 1 gram of colloid	Ammonia value (NaOH value)
	<i>Mittlemeier's</i>	<i>Mittlemeier's</i>	
Leaf mold	0.957	1.600	1.65
Clover hay	1.141	1.681	1.47
Barley straw	.457	1.274	2.79
<i>Pseudomonas fluorescens</i>	.777	1.388	1.79
<i>Alternaria</i> sp.	.215	.495	2.30
Becket soil	1.097	3.747	3.41
Marshall soil	1.288	2.680	2.08
Clover hay	1.790	2.148	1.20
Barley straw	.723	2.145	2.96
Cecil soil	.091	.193	2.01
Cecil soil, H ₂ O ₂ -treated	.057	.104	1.82
Fallon soil, H ₂ O ₂ -treated	.580	.668	1.15

These soils were treated with 5 percent NH₄OH, the extract filtered, precipitated with HCl, again altered, and the precipitate electrolyzed.

¹ The water extract was acidified with HCl and the precipitate electrolyzed.

The acidic character of the various organic colloids is very pronounced. In each case the equivalents of ammonia held exceed the amount of sodium hydroxide required for neutralization. There is considerable evidence that ammonia tends to form relatively stable salts with the colloidal organic acids, as well as with the inorganic alumino-silicic acids. The latter has been pointed out by Kelley and Brown (16) and by Puri (30). The ratio of ammonia equivalents to those of sodium varies from about 1.1 for Fallon soil colloid to 3.4 for an alkali extract of the organic portion of Becket soil. There is no regularity for this ratio within the different classes of materials. The differences in these two sets of values would seem to reflect the influence of two or more factors. In the first place, the 0.5 normal ammonium hydroxide added in considerable excess would produce a pH value much above neutrality and thus make possible reaction with secondary or tertiary acid hydrogen or other groups replaceable by bases, which are not reactive at neutrality. In the second place, there is the possibility of some ammonia being held mechanically.

The base-holding capacity of most of the organic colloids is more pronounced than that of inorganic colloids. All of them except the barley-straw colloid and the fungus material react with more base than does the Fallon colloid. The Fallon colloid, being of high silica-sesquioxide ratio (5), is itself capable of holding more base than most inorganic colloids and is several fold more effective than the Cecil colloid, even when the organic matter of the latter is not removed. The Cecil colloid is of low silica-sesquioxide ratio (3).

The organic materials which were prepared from the water extracts of organic colloids and from the alkali extracts of soils high in organic matter hold exceptionally large amounts of bases. The fact that such large quantities of ammonia are retained, presumably as ammonium salts, when the suspensions are evaporated to dryness, also indicates a considerable acid strength. This indication is more reliable than

the pH values because of the question of solubility involved in the latter case. Since the colloids of highest base-holding capacity are obtained by water extraction and by ammonia extraction, it seems evident that organic compounds of this type are subject to more rapid leaching from soils than those less marked in this respect.

On the assumption that the ammonium salts remaining after evaporation to dryness are neutral salts, the data of table 3 indicate a smaller equivalent weight for the organic colloid acids than for the electro-dialyzed inorganic colloids. It is interesting to make comparison of the equivalent weights of the organic colloids from the data obtained with the theoretical values for certain organic acids reported in various soils. For instance, uronic acid (35) with a molecular weight of 194 and monobasic, should show 5.1 base milliequivalents per gram, and hydroxystearic (34) acid 3.3 milliequivalents. No data have been obtained which either definitely establish or preclude the presence of these acids, but the presence of such materials is entirely compatible with the results. Furthermore, lignin which is present (table 2) has been shown to possess considerable base-exchange capacity (6, 9). Flax lignin prepared by the Phillips (27) method showed an ammonia-holding capacity of 0.916 milliequivalents per gram. The high values of base-exchange capacity can therefore not be due to lignin alone, unless other lignins are of much greater base-holding capacity. The equivalent weight of this compound is uncertain, but it is clear from the data that organic acids other than lignin and of higher equivalent weight than uronic acid or hydroxystearic acid are present.

The base capacities of the organic colloids are easily duplicated when made on any particular sample of material with only a short interval of time between determinations. Some evidence is at hand, however, which indicates that different preparations of colloid from a sample of decomposing material may vary widely in character. This accounts for the somewhat divergent values shown for some of the colloids in later experiments. This is in contrast with most inorganic soil colloids, of which duplicate preparations and preparations which have stood for a long time usually show relatively little difference in most of their properties.

The water-absorption capacity of soil colloids over 30 percent sulphuric acid has been shown to be a very useful property in distinguishing differences in their character. Such determinations have been made on a number of organic colloidal materials. The results are given in table 4.

TABLE 4.—Absorption of water vapor over 30 percent H_2SO_4 by various colloids

Source of colloid	H ₂ O absorbed	Source of colloid	H ₂ O absorbed
	Percent		Percent
Leaf mold ¹	15.85	Becket soil extract ¹	22.88
Clover hay ¹	14.20	Marshall soil extract ¹	16.36
Do. ²	18.98	Clover hay extract ¹	15.35
Barley straw ¹	11.74	Barley-straw extract ¹	15.18
Do. ²	16.43	Leon soil hardpan ¹	20.52
Wheat straw ¹	14.94	Peat ¹	13.73
<i>Pseudomonas fluorescens</i> ¹	10.65	Fallen soil, H ₂ O ₂ -treated ¹	18.19
<i>Alternaria</i> sp. ¹	27.43	Cecil soil, H ₂ O ₂ -treated ¹	4.76

¹ Electrolyzed material.

² Fresh colloid.

³ These materials were treated with 5 percent NH_4OH , the extract filtered, precipitated with HCl , again filtered, and the precipitate electrolyzed.

The water-absorption values ranged from 10.65 percent for the bacteria to 27.43 percent for the fungus. Debasing by electro dialysis resulted in a significant reduction in water-absorbing power amounting to about 30 percent in cases where the original material was of high base content. The absorption was of about the same magnitude as that of soil colloids, with pronounced colloidal properties, such as that from the Fallon soil. A few ran higher than any of the inorganic soil colloids which have been studied (14).

The heats of wetting of organic colloids alone are not easily determined in many cases, on account of the fact that in powder form they are usually not readily wetted by water. Determinations were made, however, of the heats of wetting of organic colloids mixed with Cecil soil colloid, the organic matter content of which was about 1.4 percent. The mixing was done by thorough agitation of the suspensions in large volumes of water slightly alkaline from the deflocculent used in the preparation of the Cecil. The results are given in table 5.

TABLE 5.—Heats of wetting of Cecil colloid mixed with various organic colloids¹

Kind of colloid or mixture	Heat of wetting per gram of material	Calculated heat of wetting per gram of organic matter	Kind of colloid or mixture	Heat of wetting per gram of material	Calculated heat of wetting per gram of organic matter
	Calories	Calories		Calories	Calories
Cecil alone.....	4.5		Cecil, 91.9 percent.....	9.3	63.8
Cecil, 91.9 percent.....	7.3	39.1	Leon (hardpan), 8.1 percent.....		
Barley straw, 8.1 percent.....			Cecil, 91.4 percent.....	6.0	22.0
Cecil, 85.0 percent.....	8.6	31.9	Bacteria, 8.6 percent.....		
Barley straw, 15.0 percent.....			Cecil, 90.9 percent.....	3.7	
Cecil, 87.9 percent.....	9.3	44.2	Fungus, 9.1 percent.....		
Clover hay, 12.1 percent.....			Cecil, 93.5 percent.....	7.4	49.2
Cecil, 85.0 percent.....	8.2	29.2	Peat, 6.5 percent.....		
Wheat straw, 15.0 percent.....			Cecil, 83.4 percent.....	11.0	43.7
Cecil, 91.0 percent.....	6.7	28.9	Peat, 16.6 percent.....		
Leaf mold, 9.0 percent.....					

¹ Organic colloid freshly dispersed mixed with slightly alkaline Cecil colloid.

² Example of calculation $\frac{(7.3 \times 100) - (91.9 \times 4.5)}{8.1} = 39.1$ calories.

³ Not all wetted by water; some floated on the surface.

The addition of from 7 to 17 percent of undialyzed organic colloid increased the heat of wetting of Cecil colloid from its original value of 4.5 calories a gram to values ranging from 7.3 to 11 calories. When calculation is made of the heat increase due to each gram of organic colloid added, these values amount to from 22 to 63 calories.³

These values are in some cases higher than might be expected, even for substances of pronounced colloidal properties. However, most of the values are not greatly different from those calculated from data obtained by indirect methods, involving the use of hydrogen peroxide for the removal of organic matter from soil colloids of relatively high organic content. In one set of data such values ranged from 19 to 47 calories per gram of organic colloid destroyed (4).

The data at hand are insufficient to show whether or not organic colloids are capable of producing the high values indicated, or whether the mixing brings about a certain change in the character of gel forma-

¹ The data given in table 5 and the subsequently calculated values are subject to somewhat greater inaccuracy than most of the data. The organic contents were estimated from differences in loss on ignition, and no allowance is made for the influence of the ash-forming portion of the colloids.

tion making possible a higher heat of wetting than is shown by the sum of the components alone. It seems highly improbable that chemical reaction would take place to any considerable degree between materials in the condition these were at the time of mixing, although reaction is highly probable under other conditions. The soil colloid was moderately alkaline, about pH 8, from the ammonia added for its dispersion, and the organic matter was of varying pH values as it occurred in the different natural materials. The chemical reactions between organic colloids and inorganic soil colloids will be subsequently considered in detail.

RELATION OF SOIL-MAKING ORGANIC RESIDUES TO SOIL COLLOIDS

The data as a whole show that colloidal materials extracted from various rotted organic residues, as well as the remains of bacteria and fungus bodies, possess colloidal properties similar in character to materials extracted from the soil and to the properties of the organic portion of soils determined indirectly. The data obtained offer no assurance that the particular compounds in the materials studied are present, or are not present, in any considerable quantity in most soils. It is clear, however, that they are materials similar in much of their behavior to a part of the organic portion which is being added to soils by natural processes. The water-holding capacity of the fungus is probably greater than that of most organic soil colloids, while its acidic character or base-holding power is somewhat less. The water absorption by bacterial cells is a little below that of most of the other organic materials studied, while its acidic qualities are much higher than the fungus and nearly in line with those of rotted plant residues. It should be noted that the fungus and bacterial residues are fresh cellular material for the most part and probably do not correspond to their residues as finally left in soil colloids. The data at hand, taken all together, make it easily comprehensible why the properties of soils, particularly those of low colloidal property values, may be greatly altered by the presence of small amounts of organic matter.

PROPERTIES OF ORGANIC COLLOIDS IN MIXTURES

Little of a definite nature is known of the influence which organic colloids have upon inorganic colloids when mixtures are made in varying proportions, or when organic colloids are mixed with inorganic material not wholly colloidal. Some evidence leads to the inference that the part contributed by organic colloids in mixtures may, in certain cases at least, be much out of proportion to that which would result if the properties of the ingredients were simply additive. There is, of course, the possibility that the gel character of the material may be altered without a chemical change more significant than possibly a change in the state of hydration. Nevertheless it is well known that a change in gel character may result in wide differences in certain colloidal properties, such as water absorption or water-holding power, and in some indirect manner may influence other properties, usually considered to be essentially chemical, such as base exchange.

In two recent investigations Powers (28, 29) found an increase in base-exchange capacity of organic colloid as a result of mixing it

with sand grains and with soil colloid. The absorption value per gram of organic colloid increased with a decrease in the percentage of colloid present in the cases where quartz sand was used. When soil colloids were used maximum values were reached with 20 to 40 percent of organic colloid present.

There is no rational basis for assuming any kind of interaction between organic colloid and quartz sand grains. The presumption is, therefore, that the change in state of aggregation resulting from a distribution over sand grains made it more reactive with the barium chloride solution used in these experiments. There is, of course, also the possibility that an increase in the rate at which the washing could be carried out might alter the quantity of cations left with the colloidal organic acid after the excess of electrolyte was removed. There is therefore an element of doubt as to whether or not the determinations are strictly comparable. Several papers by Demolon and associates (11, 12) show some form of "fixation" of humus and other organic substances by clay. The type of interaction involved is not clear, but the presumption is that chemical forces were involved to some extent at least.

Humic acid, or more strictly speaking, the various acids of this type which are soluble in alkalis and precipitated by acids, have been prepared and studied by many investigators over a long period. In some cases these acids have probably been used in a form approximating true solutions of their salts. In other cases essentially colloidal material in the form of the very slightly soluble acids has been employed. One would expect differences in the behavior of soluble salts of humic acid, the more distinctly acid form of humus in colloidal form, and the other colloidal organic matter not usually classified as humic acid. This seems in general to be the case.

Kawamura (15) treated humic acid from peat and from cane sugar with bases and found that the samples behaved similarly; 1 gram of the humus took up about 3 equivalent millimols of base. Both forms of humic acid absorbed aluminum from aluminum chloride and almost no chlorine. The aluminum remained in the complex after washing free from chlorine and showed exchange acidity. The composition of the material was such as to suggest the formation of aluminum trihumate.

In this study of the colloidal character of organic colloids, which have some relationship to soil organic matter, certain mixtures have been investigated. Some of the same determinations were made as were used in the study of organic colloids alone, particularly the determinations of water vapor absorption and the absorption of ammonia. Preliminary results showed fairly good agreement of duplicates in most cases, but the results were erratic when one mixture was compared with another. A few determinations of base-exchange capacity by the use of the barium chloride method were made, but these results are not included. The duplicates were poor, presumably due to the difficulty of comparable washing when the colloids of the mixtures varied in porosity and permeability. No attempt was made to solve the difficulties of this determination since essentially the same type of information could be obtained by the ammonia absorption determination as previously described; a determination which appears to be beset by less fundamental difficulties.

WATER-VAPOUR ABSORPTION BY COLLOID MIXTURES

In the study of water-vapor absorption by the mixtures of organic colloid with quartz flour or with inorganic soil colloid, samples of well-dispersed colloid were used and the mixing done by shaking or by agitation in a Buoyoucos agitator. The materials were then dried, pulverized, and the water-vapor absorption determined in the usual manner. A preliminary set of results are given in table 6.

TABLE 6.—Absorption of water vapor over 50 percent H_2SO_4 by various colloids and mixtures of the colloids with other substances

Kind of material ¹	Water vapor absorbed	Calculated absorption of mixture if unchanged	Change resulting from mixing	Calculated absorption of organic colloid in mixture
	Percent	Percent	Percent	Percent
Leaf mold.....	15.85			
Clover hay.....	14.20			
Barley straw ²	16.43			
Do.....	11.74			
Quartz flour.....	11			
Cecil soil.....	4.76			
Quartz flour, 97.5 percent.....	.58	0.61	+13.7	18.8
Leaf mold, 2.5 percent.....	1.29	1.10	+17.3	18.9
Quartz flour, 93.7 percent.....	.63	.49	+28.6	19.3
Leaf mold, 6.3 percent.....	1.35	1.20	+4.7	14.9
Quartz flour, 97.3 percent.....	18.10			
Clover hay, 2.7 percent.....	1.74	1.63	+6.7	
Quartz flour, 91.6 percent.....	16.47	17.79	-7.4	(?)
Fallon soil, 6.4 percent.....	16.34	17.92	-8.8	(?)
Fallon soil, 93.1 percent.....	5.26	5.83	-10.5	10.00
Clover hay, 9.9 percent.....	4.71	5.23	-9.9	3.7
Fallon soil, 88.8 percent.....	4.97	5.45	-8.8	6.9
Leaf mold, 11.2 percent.....	5.34	5.79	-7.8	8.6
Cecil soil, 90.4 percent.....				
Barley straw, 6.3 percent ³				
Cecil soil, 95.1 percent.....				
Barley straw, 4.9 percent ³				
Cecil soil, 85.2 percent.....				
Barley straw, 14.8 percent.....				
Cecil soil, 85.2 percent.....				
Barley straw, 14.8 percent.....				

¹ The materials listed in this column are all colloids except the quartz flour, a considerable part of which was of colloidal dimensions.

² Not electrolyzed.

³ None.

The results in table 6 are of value in pointing out general relationships in spite of the fact that they are very inconsistent from a quantitative standpoint. Duplicate absorption determinations were run on each mixture prepared, and these were in fairly good agreement but sometimes not so good as when single substances are used. This does not mean, however, that a second preparation with the same quantities involved would necessarily agree as closely. Two significant facts stand out. (1) Organic colloid mixed with quartz flour results, in every case, in an increase in water absorption over that calculated for the constituents taken alone, and (2) organic colloid shows a reduction in water absorption as a result of mixing with a soil colloid; that is, the absorption of the mixture is less than the sum of the constituents taken alone. The variations are not consistent in either case; in fact, it would be surprising if they were consistent

in all cases for the distribution of the colloid throughout the mass could hardly be uniform even when the same quantities are present. A significant factor in this connection may be the condition of the electrodyalized acid colloids. These were in reality somewhat coagulated even though they stayed in suspension for several hours after agitation. It seems highly probable in the case of quartz flour and colloid that the porosity of the quartz aided in the accessibility of the water to the colloid. This explanation applies also to a sample of the highly absorbing Fallon soil colloid, which behaved in quartz similarly to the organic colloids. Furthermore, when soil colloid was added to organic colloid, the reduced absorption was probably due in part to poorer accessibility of water to the organic colloid and in part to some form of chemical action between the organic acid and the soil colloid, whereby a gel of somewhat different character was formed.

AMMONIA ABSORPTION BY COLLOID MIXTURES

The ammonia-absorption determinations made in the first section of this bulletin were carried out with only ordinary care as to the conditions of drying. Numerous determinations of organic colloids and of soil colloids alone showed that drying on a steam bath for 1 to 5 hours or heating at 75° to 80° C. had but little effect upon the quantity of ammonia held. The results shown in table 7 indicate from their irregularity that much more care must be taken in regulating the conditions of drying in the case of certain mixtures.

TABLE 7.—Ammonia absorbed by various colloids alone and in mixtures

Kind of colloid	Ammonia absorbed per gram of material	Calculated absorption per gram of mixture if constituents remain unchanged	Absorption per gram of organic colloid calculated	Alteration of combined constituents resulting from mixing
	Milli-equivalents	Milli-equivalents	Milli-equivalents	Percent
Clover hay.....	1.717			
Leaf mold.....	1.600			
Fallon soil.....	.568			
Cecil soil.....	.183			
Do ¹104			
Quartz flour ¹	(²)			
Bacteria.....	1.388			
Fallon soil, 44.4 percent.....	.372	0.398		-6.5
Cecil soil, 55.6 percent.....				
Fallon soil, 69.0 percent.....	.154	.166		-7.2
Cecil soil, 11.0 percent.....				
Fallon soil, 88.8 percent.....	.766	.772	1.55	-8
Leaf mold, 11.2 percent.....				
Fallon soil, 90.1 percent.....	.779	.772	1.80	+9
Clover hay, 9.9 percent.....				
Cecil soil, 93.8 percent.....	.243	.270	1.16	-10.0
Leaf mold, 6.2 percent.....				
Quartz flour, 97.3 percent.....	.024	.046	.89	-48.0
Clover hay, 2.7 percent.....				
Quartz flour, 91.6 percent.....	.077	.144	.92	-48.0
Clover hay, 8.4 percent.....				
Quartz flour, 97.5 percent.....	.030	.040	1.20	-25.0
Leaf mold, 2.5 percent.....				
Quartz flour, 93.7 percent.....	.056	.101	.89	-45.0
Leaf mold, 6.3 percent.....				
Bacteria, 3.8 percent.....	.115	.152	.29	-24.0
Cecil soil, 96.2 percent.....				
Bacteria, 7.0 percent.....	.161	.194	.90	-10.0
Cecil soil, 93.0 percent.....				
Bacteria, 10.5 percent.....	.205	.228	.89	-14.0
Cecil soil, 89.5 percent.....				

¹ Treated with H₂O₂ before electrodyalisis. ² Very fine material but only partly colloidal. ³ Trace.

Although the ammonia reaction may be assumed to be more definitely chemical in character than the absorption of water vapor, it appears to be affected by some of the same factors, namely, state of aggregation and the exposure of its surfaces in a variable manner. These factors may be responsible for much of the variation. There seems to be no reason for assuming a reaction of any kind between quartz flour and acid colloid which would significantly diminish the acid character of the latter.

In view of the results given in table 7 and of other data which will be shown in a later table, it seemed highly desirable to learn whether or not, by very rigid adherence to comparable conditions, more consistent results could be obtained. A freshly electrodyalyzed and homogenized sample of the rotted oak-wood colloid was measured out in 10 cm³ portions from a pipette having a large tip. The organic colloid thus measured was added to varying quantities of very fine quartz flour in portions of 5, 10, and 15 grams per sample. The samples were thoroughly stirred and each treated with about 20 cm³ of 0.5 normal ammonium hydroxide in 100 cm³, then allowed to evaporate very slowly on a steam bath. After dryness was reached a second portion of ammonia was added. As soon as the samples became dry they were removed from the steam bath and placed in an oven at 75° C. for 5 hours. Distillation with magnesium oxide was then carried out in the usual manner. The results are shown in table 8.

TABLE 8.—*Influence of sample and presence of quartz flour upon the absorption of ammonia by rotted wood colloid*

Weight of sample	Constituents	Organic colloid present	Ammonia absorbed by whole colloid	Calculated absorption per gram of organic colloid	Loss resulting from mixing
Grams	Percent	Grams	Milli-equivalents	Milli-equivalents	Percent
0.431	-----	0.431	0.495	1.15	-----
.862	-----	.862	1.054	1.22	-----
1.293	-----	1.293	1.549	1.20	-----
15.431	2.1 percent organic colloid.....	.431	.444	1.03	10.3
	97.9 percent quartz flour.....				
10.431	4.1 percent organic colloid.....	.431	.438	1.02	11.3
	95.9 percent quartz flour.....				
5.431	7.9 percent organic colloid.....	.431	.438	1.02	11.3
	92.1 percent quartz flour.....				
5.862	14.7 percent organic colloid.....	.862	.917	1.06	13.1
	85.3 percent quartz flour.....				
5.293	20.6 percent organic colloid.....	1.293	1.404	1.14	5.2
	79.5 percent quartz flour.....				

It is evident from the data presented that variations due to size of sample within the limits investigated are but little more than might sometimes be obtained by duplicates in this type of base-exchange reactions. However, there is a tendency toward lower results with small samples and moderately lower results when any quartz is present. When relatively large quantities of quartz flour were present the ammonia absorption was reduced by approximately 10 percent. The samples of mixtures used in this set of determinations were much larger than those used in the other experiments. Samples of 0.7 gram to 4.0 grams each of colloids, depending upon the absorbing power, were found to be satisfactory in the earlier experiments with soil and

organic colloids alone. It is evident, however, that in certain cases closely similar sample size is necessary for the duplicate results.

It is difficult to evaluate definitely the different factors which may have an influence upon ammonia-absorption values in such mixtures. Even though there may be a difference in the surface exposed as a result of mixing a colloid with an inert substance, it is still not clear whether the lower ammonia values result from greater desiccation or from decomposition of the dry compound, independent of the water content.

From the results thus far presented there is no basis upon which to decide whether the alteration in ammonia absorption in the soil colloid-organic colloid mixtures is due to causes similar in nature to those operative with quartz flour, or whether a more or less definite chemical reaction had taken place between the sesquioxides of the soil colloid and the colloidal organic acid whereby the absorbing power of the latter was lowered. The fact that the Cecil colloid doubtless contains more or less free sesquioxides and the possibility of a reaction between the acid organic matter and one or both of these oxides is entirely compatible with the results. It seemed desirable, therefore, to study this possibility in greater detail.

HYDRATED OXIDES AND ACID ORGANIC COLLOIDS

Various investigations have pointed to the probability of some degree of chemical interaction between sesquioxides and soil organic matter. Experiments which have heretofore been made on this subject have concerned for the most part studies of coagulated mixtures of organic matter with sesquioxides in varying proportions. Coagulation of mixtures of colloids does not of course necessarily imply any extensive chemical interaction but may be the neutralization of the opposite charges which served to stabilize the separate colloids.

The studies of Aarnio (1) showed that ferric hydroxide² sols mixed in varying proportions with organic matter sols from different peats brought about complete flocculation over considerable range of composition. Although the results varied widely, depending upon the conditions of the experiments, certain generalizations may be made. An average taken from a number of Aarnio's results showed precipitation beginning when the proportions of Fe_2O_3 to organic sol was 1 : 1.65 by weight and ending when the ratio was 1 : 0.47. A single experiment using alumina instead of iron showed a ratio of 1 part Al_2O_3 to 30 parts of organic sol at the beginning of precipitation and a ratio of 1 : 1 when precipitation ended. It is evident that, as a rule, much more organic sol is required to precipitate alumina than is required for sols of ferric hydroxide but that the range of proportions over which precipitation is complete is greater in the case of alumina.

The results of Mattson's research (20, 21), while not directly comparable with those of Aarnio, show in general that larger quantities of organic matter are required to form a precipitate with aluminum chloride than with ferric chloride. Furthermore, Mattson calls attention to the possibility of flocculating mixtures of sesquioxides with organic sols in any proportion, provided the proper pH values are attained by the addition of either acid or alkali. Subsequent

² It is of course recognized that ferric hydroxide may easily lose water and become ferric oxide more or less hydrated.

work by Mattson (23) shows a relationship between composition, flocculation, and pH value of mixtures of sesquioxides with proteins and with humus.

In order to test further the manner and degree to which free sesquioxides would function if present in the colloid system containing organic matter, experiments were made, using highly purified alumina and hydrated oxides of both ferrous and ferric iron and of silicic acid. The alumina and the ferric hydroxide were prepared by neutralizing solutions of the respective chlorides, washing by the use of Pasteur-Chamberland filters until the chloride contents were low, then electro dialyzing to remove all but a minute trace of chloride. These hydrates were then drawn through a Gooch crucible to produce a well homogenized condition and this material, without previous drying, was thoroughly mixed with the organic colloids and the ammonia and water absorption determined (tables 9, 10, 11).

TABLE 9.—Ammonia held by organic colloids, by $Al(OH)_3$, and by mixtures

Source of colloid and percentage of $Al(OH)_3$ used	Ammonia absorbed per gram of colloid	Calculated absorption by mixture assuming constituents unchanged	Calculated absorption of organic colloid in mixture
	Milli-equivalents ⁽¹⁾	Milli-equivalents	Milli-equivalents
$Al(OH)_3$			
Barley straw.....	1.000		
Oak wood.....	1.085		
Barley straw, 10 percent.....	.025	0.100	0.250
$Al(OH)_3$, 80 percent.....	.025	.100	.250
Barley straw, 10 percent.....	.025	.100	.250
$Al(OH)_3$, 90 percent.....	.068	.200	.330
Barley straw, 20 percent.....	.068	.200	.330
$Al(OH)_3$, 80 percent.....	.068	.200	.330
Barley straw, 20 percent.....	.031	.088	.183
$Al(OH)_3$, 81.9 percent.....			
Oak wood, 3.3 percent.....			
$Al(OH)_3$, 81.9 percent.....			
Oak wood, 3.3 percent.....			
$Al(OH)_3$, 98.7 percent.....	(1)	.036	.212

¹ None.² Duplicate preparation of $Al(OH)_3$.³ Trace.

TABLE 10.—Influence of the presence of ferric hydroxide upon the ammonia absorption of electro dialyzed organic colloids

Percentage of colloid and of ferric hydroxide used	Ammonia absorbed per gram of organic matter	Loss resulting from mixing	Percentage of colloid and of ferric hydroxide used	Ammonia absorbed per gram of organic matter	Loss resulting from mixing
	Milli-equivalents ⁽¹⁾	Percent		Milli-equivalents	Percent
Ferric hydroxide, 100 percent.....			Peat, 19.6 percent.....		
Barley straw, 100 percent.....	1.00		Ferric hydroxide, 80.4 percent.....	1.50	32.5
Barley straw, 10 percent.....	.94	6.0	Peat, 10.9 percent.....		
Ferric hydroxide, 90 percent.....	.91	9.0	Ferric hydroxide, 89.1 percent.....	1.57	32.0
Barley straw, 10 percent.....	.91	9.0	Rotted wood ²	1.10	
Ferric hydroxide, 90 percent.....	2.71		Rotted wood, 36.2 percent.....	.79	28.2
Humic acid, 100 percent.....	2.22	18.1	Ferric hydroxide, 63.8 percent.....		
Humic acid, 27.6 percent.....	2.31		Rotted wood, 19.8 percent.....	.64	41.8
Ferric hydroxide, 72.4 percent.....	2.09	2.5	Ferric hydroxide, 80.2 percent.....	.56	47.8
Peat, 100 percent.....	1.79	22.5	Rotted wood, 15 percent.....	.52	62.7
Peat, 40.4 percent.....			Ferric hydroxide, 85 percent.....		
Ferric hydroxide, 59.6 percent.....			Rotted wood, 11.3 percent.....		
Peat, 36.9 percent.....			Ferric hydroxide, 88.7 percent.....		
Ferric hydroxide, 63.1 percent.....					

¹ None.

² This is an aliquot of the above sample which stood for 3 months drying slowly before addition of NH_4OH .

³ Humic acid was prepared from Trencary fine sandy loam soil by extraction with NH_4OH , evaporation, and subsequent electro dialysis.

⁴ The determinations with rotted wood and those with peat were made at one time, each mixed and dried for the same period, and the members of each set had identical weights of organic colloid.

TABLE 11.—Absorption of water vapor over 30 percent H_2SO_4 by various electro-dialyzed colloids alone and in mixtures

Kind of colloid or mixture	Water vapor absorbed	Calculated absorption of mixture if unchanged	Change resulting from mixing ¹	Calculated absorption of organic colloid in mixture ¹
	Percent	Percent	Percent	Percent
Ferric hydroxide.....	11.89			
Alumina (no. 1).....	.99			
Alumina (no. 2).....	2.50			
Silica.....	18.32			
Barley straw.....	11.99			
Cecil soil.....	4.18			
Ferric hydroxide, 90 percent.....	12.23	11.90	+2.8	15.3
Barley straw, 10 percent.....				
Ferric hydroxide, 80 percent.....	9.25	11.90	-22.9	(²)
Barley straw, 20 percent.....				
Alumina B, 90 percent.....	3.97	3.45	+15.1	17.2
Barley straw, 15 percent.....				
Alumina B, 80 percent.....	4.49	4.40	+2.0	12.5
Barley straw, 20 percent.....				
Silica, 90 percent.....	17.63	17.68	.0	12.9
Barley straw, 10 percent.....				
Silica, 80 percent.....	18.82	17.65	-1.3	10.8
Barley straw, 20 percent.....				
Cecil soil, 90 percent.....	4.71	4.96	-5.0	9.5
Barley straw, 10 percent.....				
Cecil soil, 80 percent.....	5.04	5.74	-13.9	8.5
Barley straw, 20 percent.....				

¹ Absorption by inorganic colloid is assumed constant.² None.

Included in this study also was a sample of silicic acid prepared from sodium silicate and hydrochloric acid and purified in a manner similar to that used in the preparation of the hydroxides of iron and of aluminum, except that in the case of silica the material was dried on a moderate steam bath once before purification was complete. Removal of electrolytes from the highly dispersed silica was so slow as to make it impractical to complete purification of a considerable quantity without drying.

Several problems arose in connection with the determination of the ammonia absorbed by these materials. There is no difficulty in the determination with alumina alone as an absorbent. Samples of different weights, dried in different ways, all showed zero or very small values. In the case of ferric hydroxide difficulty in securing duplicate results was encountered when the earlier procedure of drying was used, that is, a single drying on the steam bath. The ferric hydroxide held tenaciously to very significant quantities of ammonia, whether dried on the steam bath, in the oven at 80° C., or in the oven at 105°. The values for the iron compounds alone varied from zero to as much as 250 milliequivalents per gram. However, it was found that by drying the substance for 5 hours at 75°, then again moistening with ammonia and repeating the drying process, the results were consistently near zero. It is not clear whether ammonia was held by the water content of the ferric hydroxide, whether an ammonium compound of a fair degree of stability was formed, or whether some other form of absorption was responsible for the behavior of the ferric hydroxide in a manner very different from that of alumina.

Silicic acid presents the same type of experimental difficulties as the ferric hydroxide as regards the ammonia held, but no standard conditions of drying have been found which will give satisfactory results

with this material and at the same time not be too drastic for other colloids which might be mixed with the silica. Determination of ammonia absorption for silica alone varied from 0.024 to 0.206 milliequivalent, and the results were not reliable for any set of conditions. A preliminary experiment with silica and organic colloid gave the same type of erratic results, and no attempt was made to carry further a study of the possible reaction between organic matter and colloidal silica by ammonia absorption. The indications were that varying degrees of dehydration gave forms of silicic acid varying in strength, in accessibility to reaction, and in stability of the ammonium salt. The ammonia absorption by mixtures of alumina and organic matter are given in table 9 and mixtures of ferric hydroxide and organic matter in table 10.

From 65 percent to nearly the entire ammonia-absorbing power of two kinds of organic matter were destroyed by mixing with alumina in varying proportions. This is not surprising in view of the fact that an excess of hydroxyl ions are shown by the purified alumina. The pH values of this material vary but are ordinarily found to lie within the range 7.7 to 8.2, averaging about 8.1.

It is of course not possible on this basis to predict with any certainty the extent to which a colloidal acid would react with a colloidal base of this kind in view of the very low solubilities involved. Nor is it possible to predict the manner or extent to which the surface of either of these might be rendered inactive by one of them covering the other. In line with this consideration the pH values of ferric hydroxide suspensions determined here, and also those given by Mattson (20), range from about 6.8 to 7.2. In this respect they cannot be regarded as furnishing any significant excess of hydroxyl ions. The results are consistent with what might be expected from mixing a neutral colloidal material with an acid one; that is, no significant reduction of the ammonia-absorbing power of the organic colloid took place. A considerable number of determinations with organic matter and ferric hydroxide were made which are not included here because of the erratic results. However, it is felt that the last results obtained (those when the conditions of drying and other procedure mentioned on page 15 were closely followed) are sufficiently accurate to justify the conclusion that there is very little or no interaction between ferric hydroxide and acid colloidal organic matter and that compounds, if formed, are relatively unstable. It is perhaps not safe to offer this conclusion without some reservations, for it is true that in some cases the drop in ammonia absorption resulting from mixing is distinctly greater than when organic mixtures are made with quartz flour. However, the porosity of the ferric hydroxide may be much greater and this may be a factor in making the difference. It must be considered also that the work of Burk and associates (6, 7) indicates the presence of a compound formed between humic acid, apparently in true solution, and the ferric ion when mixtures are made with ferric sulphate in solution. Their solutions, however, were very acid.

A further link in the chain of evidence that ferric compounds of colloidal humic acids, if formed, are very unstable was obtained by electrometric titration of a sample of colloidal humic acid alone and a duplicate sample mixed with ferric hydrate 2 days previous to the addition of sodium hydroxide. The humic acid used was the electrolyzed fraction of material extracted by ammonium hydroxide

from Trenary soil, a part of the sample described in table 14. The humic acid alone gave a titration value, at pH 7.0, of 0.99 milliequivalent of Na per gram of colloid. Equilibrium was reached in less than 30 minutes and remained practically unchanged on standing over night. When the same weight of humic acid was used in a mixture containing 27.6 percent humic acid and 72.4 percent ferric hydroxide, a pseudoequilibrium was reached at the end of an hour in the electrometric titration, at which time the NaOH used was 0.67 milliequivalent per gram of organic matter. The next day the pH value had receded to 5.6 and a total of 0.97 milliequivalent of NaOH was necessary to attain a true permanent approximate equilibrium at pH 7.0. In other words, the presence of ferric hydroxide had no permanent effect upon the titration value of the humic acid.

WATER-VAPOR ABSORPTION BY SYNTHETIC GEL MIXTURES WITH ORGANIC COLLOIDS

The absorption of water vapor over 30 percent sulphuric acid was determined upon samples from the mixtures used in the study of the ammonia absorption shown above. The water-vapor absorption results are given in table 11.

It is evident that water-vapor absorption is a very poor criterion of chemical interaction in the case of organic colloids and synthetic gels, partly because the gels alone show such wide variation in absorption, depending upon method of preparation and manner of drying. The two samples of alumina whose water-vapor absorption is shown in table 11 were prepared in like manner except that sample no. 1 was air-dried before electrodialysis and had stood for several months, while sample no. 2 was kept in a creamy condition until drying just before the absorption determination was made. Other fractions of the silica preparation also showed considerable variation not given in the table and the presumption is that ferric hydroxide would likewise vary. The irregularities of this class of data are in line with the varying physical character which may occur where mixed gel materials are coagulated together.

REACTIONS OF ORGANIC COLLOIDS WITH FERROUS HYDROXIDE

Since alumina apparently reacted much more markedly with acid colloidal organic matter than did ferric hydroxide, it seemed of interest to determine whether or not the more soluble and stronger base, ferrous hydroxide, would be even more reactive than alumina. If so, this reaction would be of importance in interpreting certain soil-development processes.

Two independent preparations of ferrous hydroxide were made by the same procedure. Ferrous ammonium sulphate solution was placed in the middle chamber of a Bradfield type electrodialysis cell. This was kept in an atmosphere of hydrogen while ammonia was introduced to precipitate ferrous hydroxide and the ammonium and sulphate ions were removed by electrodialysis. Several days were required to purify this material. In the process a considerable quantity of the iron was lost by passage through the cellophane membranes. The exclusion of oxygen was not perfect, hence a very small amount of oxidation took place. In order to carry out the absorption determination, a portion of the ferrous hydroxide was

forced over by hydrogen pressure into an iron reduction flask containing a definite quantity of dispersed organic colloid. After thorough mixing, ammonia was introduced and a flow of hydrogen continued until the flask reached constant weight on a steam bath. From this weight the quantity of ferrous hydroxide introduced was calculated. The contents of the flask were then distilled with magnesia in the usual way. The results contrasted so markedly with those of ferric iron that an attempt was made to see if the mere process of oxidation would restore the ammonia-absorbing power of the organic colloid after the mixture with ferrous iron. Samples were therefore prepared in the manner previously described, but before distilling 200 cm³ of water were added and air bubbled through until the contents were dried on the steam bath under conditions similar to those used before oxidation. The results are given in table 12.

TABLE 12.—Ammonia held by organic colloids, ferrous hydroxide, and by mixtures

Kind of colloid and percentage of ferrous hydroxide used	Ammonia absorbed per gram of colloid	Calculated absorption of mixture assuming constituents unchanged	Kind of colloid and percentage of ferrous hydroxide used	Ammonia absorbed per gram of colloid	Calculated absorption of mixture assuming constituents unchanged
	Milli-equivalents (1)	Milli-equivalents		Milli-equivalents	Milli-equivalents
Ferrous hydroxide.....			Oak wood, 16.6 percent, after oxidation.....		
Do. ¹			Ferrous hydroxide, 83.4 percent, after oxidation.....	0.336	0.166
Barley straw ²	1.000		Oak wood, 11.9 percent.....		
Oak wood.....	1.585		Ferrous hydroxide, 88.1 percent.....	.027	.119
Barley straw, 13.1 percent.....		0.131	Oak wood, 11.9 percent, after oxidation.....		
Ferrous hydroxide, 86.9 percent.....			Ferrous hydroxide, 88.1 percent, after oxidation.....	.103	.119
Barley straw, 20.7 percent.....	.013	.207			
Ferrous hydroxide, 79.3 percent.....					
Oak wood, 76.4 percent.....					
Ferrous hydroxide, 23.6 percent.....	.072	.829			

¹ None.² Duplicate determination with a fresh preparation of material.³ Trace.⁴ Special preparation.

The ammonia results strongly indicate a reaction between the colloidal organic matter and ferrous hydroxide. This is not surprising in view of the very appreciable solubility of ferrous hydroxide and its alkaline reaction. No attempt was made to determine definitely the pH values of the ferrous hydroxide suspensions but qualitatively they were distinctly more alkaline than those of either alumina or ferric hydroxide. It would seem that the colloidal organic acid reacted with the ferrous hydroxide to form a more or less definite type of complex whose reaction approximated neutrality or at least was not sufficiently acid to hold significant quantities of ammonia until the proportions of organic matter to ferrous hydroxide became very large. On oxidation the ferric salt, containing a much weaker base than the ferrous one, was formed and, by hydrolysis, there was a strong tendency toward the formation of free ferric hydroxide and the original type of colloidal organic acid. While the

ammonia results indicate this type of reaction, it must be kept in mind that it is hardly safe to ascribe all of the absorption after oxidation as necessarily coming from the organic acid, for it is very difficult by this procedure to be entirely certain that some part of it might not be from retention of the ammonia by the ferric hydroxide. However, the magnitude of change leaves little doubt that ferrous salts of colloidal matter are reasonably stable in a reducing atmosphere and that the ferric salts probably split and deposit iron in the form of hydrated oxides.

THE ROLE OF ORGANIC COLLOIDS IN SOIL-PROFILE FORMATION

The difference in the behavior of ferrous iron and that of the ferric form when in contact with acid organic material appears to be an important factor in the development of the podzol type of soil profile. It may be assumed that in the hydrolysis of silicate minerals containing ferrous iron, such as hornblende and many others, ferrous hydroxide is produced. Under high humidity the decomposing organic matter is debased to a very acid condition. The humic acid thus formed reacts with the ferrous hydroxide, forming a compound which is carried downward either in solution or in a high state of dispersion by the percolating water. This salt, while being subjected to continued oxidation during the process of its movement, encounters less acid conditions as it moves downward where the minerals are less decomposed. The ferrous humate is then precipitated, hydrolyzed, and oxidized to form primarily a mixture of ferric hydroxide and humic acid characteristic of the B horizons of most podzol profiles. As a rule the percentage of organic matter is relatively high in the upper part of the B horizon, showing a tendency for a part of the organic portion to be precipitated more easily than iron. However, it is well known that a part of the organic matter in various types of soil profiles often escapes the precipitating influences of oxidation, filtration, and pH changes, and is carried down to considerable depths disseminating itself deep in the C horizon material which is penetrated little or not at all by plant roots.

Attention has been called previously to the concentration of iron oxide as compared to aluminum as a characteristic feature of the podzolic process of soil development, the difference usually being very pronounced in the typical podzol profiles (8). The reaction of alumina with the various humic acid complexes compared with the action of iron compounds with these indicates the probable chemical basis upon which these profile characteristics depend. While rather abrupt changes in the character of the iron compounds take place with oxidation, the alumina is not affected by this factor, changes in alumina depending more upon changing pH values and the filtering process through a medium of varying porosity.

AMPHOTERIC CHARACTER OF SOIL ORGANIC MATTER

It is well known that soil organic matter gives evidence of possessing a strong buffer capacity. Changes in the pH values of a soil upon additions of acid or alkali are usually much less pronounced where a considerable amount of normal soil organic matter is present than where the soil consists almost entirely of inorganic material (10, 17) even though the inorganic portion may itself be well buffered. This,

of course, means that soil organic matter reacts to some extent at least as a base, as well as showing its predominating acid character.

In the study (p. 9) of the organic colloids from soils and from soil-making organic materials attention has been directed to their behavior as weak bases as well as their more familiar reactions as moderately strong but only slightly soluble complex acids. Studies of this kind are ordinarily very much complicated by the presence of the soil which is itself amphoteric, and its amphoteric character is known to vary widely with the degree to which the original minerals have undergone hydrolytic changes (22, 24).⁴ Methods of separating organic colloids from the inorganic matter with any considerable degree of completeness without drastic treatment has not been satisfactorily accomplished. In the present studies fractions comprising very substantial portions of the organic matter of certain soils have been separated in widely different manners, depending to a considerable extent upon their amphoteric character, and these fractions studied and compared.

In the study of the various organic colloids many observations of a preliminary nature have contributed to the procedure of fractionation finally undertaken in detail. Some of these are detailed below.

In the process of dialysis of neutral or alkaline organic soils and of decomposed organic residues a certain amount of the dark-colored organic material diffuses through such semipermeable membranes as are ordinarily used. This of course gives no idea as to the chemical character of the material except to indicate that a part of it has the character of a sufficiently simple solution to pass through the membranes. When a colloid of this kind is placed between two semipermeable membranes and an electric current passed through, as in the process of electrodialysis, additional information is obtained. It is well known that in certain stages, at least, of electrodialysis considerable material of a dark color passes into the anode chamber, together with other anions. The presumption is that this material is very definitely acidic. In the cathode chamber there is very little color, provided the colloid is neutral or alkaline at the beginning. Several tests showed, however, that measurably more carbon was present in the cathode chamber when organic colloids were present than when a current was passed through the membranes in the absence of the organic colloid. Tests were made using both parchment and parchment paper, each of which gave significant quantities of carbonaceous material passing into each chamber from the membranes alone. This work was done before the use of cellophane membranes was adopted.

ACID TREATMENT OF ORGANIC SOIL COLLOIDS

Although there was an indication of some organic material existing in the form of diffusible cations, there was no evidence from the electrodialysis experiments with untreated organic matter to indicate that the quantity involved was any significant part of the whole of the organic matter.

The method of Rather (31) for the determination of soil organic matter is based upon the decomposition and solution of the hydrous

⁴ BYERS, H. G. THE CHEMICAL CONSTITUTION OF SOIL COLLOIDS. Amer. Soil Survey Assoc. Rpt. Ann Meeting 13, Bul. 14, p. 47-52, illus. [Micrographed.]

inorganic matter by hydrofluoric and hydrochloric acids, each of a strength of 0.5 percent, while the accompanying solution of organic matter was found in his experiments to be very small. In the work by Alexander and Byers (2), who used a 5 percent acid solution, the loss of organic matter by solution was more marked. Nevertheless, it seemed desirable to determine whether or not a fraction of organic colloid practically free from inorganic material could be prepared by removal of inorganic colloid by this method.

The colloidal materials from the B horizons of many podzol soils are of relatively high organic-matter content, therefore, a sample from the B horizon of the Becket soil series was selected on which to test the principle of Rather's method for the purpose of preparing a fraction of organic colloid relatively free from ash constituents. An acid mixture was used containing 2 percent H_2F_2 and 2 percent HCl. A 140-gram sample of colloid was used which showed an initial loss on ignition of 30.7 percent. The solution turned black immediately when the acids were added. After treating and decanting four times, the loss on ignition of the residue was 38.4 percent. After 9 washings, the last 3 of which were digested on a steam bath, there was a residue of only about 10 grams. Approximately 2 grams had been previously removed for intermediate tests. The loss on ignition of the final residue was 82.2 percent.

Wabash soil colloid, a subsample of the material described in a former publication (33) was treated once with about 100 times its weight of the acid mixture described above. The residue showed a loss on ignition of 63 percent compared with about 12 percent for the untreated material.

These preliminary qualitative experiments indicate a very considerable solubility of the colloiddally dispersed organic materials. They show that in the case of the podzol soil, in particular, the solution of organic matter in acids is too great to make practical the removal of the inorganic portion by the procedure used. There is indication, however, that strong acids, such as hydrochloric acid, in moderate concentration are capable of dissolving very considerable quantities of organic colloids, presumably in the form of chlorides of complex organic cations.

HYDROCHLORIC ACID EXTRACT

In order to test further the acid solubility of soil organic matter, Becket soil was extracted with 2 percent hydrochloric acid and the extract dialyzed between cellophane membranes for several days with frequent removal of the dialysates. In a short time a precipitate was formed which increased in quantity as the acid concentration was reduced. Finally the partly dialyzed material was subjected to electrodialysis. A dark-colored dialysate appeared very quickly in the cathode chamber of the dialyzer while one of lesser color appeared in the anode. As the process continued the color of cathode dialysates became less intense and those at the anode became colored more nearly as those from untreated materials. When freed from chlorine ions the electrodialyzed material was subjected to chemical examination, together with other samples which will be described later.

SULPHUROUS ACID EXTRACT

Most of the strong mineral acids, while dissolving large quantities of organic matter, are nonvolatile except when highly concentrated. It is, therefore, necessary to remove the excess of acid by dialysis in which case large quantities of organic material dialyze through the membranes. In order partly to overcome these difficulties extraction was made with saturated solutions of sulphur dioxide, which forms a fairly strong acid readily decomposed by heat without concentration at any time. When sulphur dioxide was bubbled into a suspension of the Becket soil the solution turned dark in a short time. The clear extract, after filtration, gave a copious brown precipitate on boiling. This precipitate, after electrodialysis, had an ash content of from 15 to 25 percent, varying considerably with the time and extent of extraction. The amount of material removable in this manner is very considerable. It seemed desirable, therefore, to prepare fractions by solution in this reagent and compare the composition and properties of such fractions with fractions extracted in a conventional manner by ammonia. Fractions were prepared in like manner from different soils in order to see what indication could be found of similarities and differences in the character of organic matter in different soils.

FRACTIONATION OF SOIL ORGANIC MATTER

On the basis of information obtained from the preliminary experiments four fractions of organic matter were extracted from each of three soils. Details of the procedure follow: Samples of 500 or 750 grams each of soil were extracted with a total of about 8 to 10 liters of saturated sulphur-dioxide solution, allowing each liter portion to stand in contact with the soil several hours. The treatment used did not remove all of the organic matter extractable by the reagent, but the extraction reached a point where the amount removed was small and the inorganic matter was dissolved at a much greater rate compared to the organic than at first. Further extraction would have served to progressively increase the ash content of the fraction. After each extraction the liquid was filtered through Pasteur-Chamberland filters and the clear solution evaporated by boiling to about one third the original volume. The precipitate which formed was allowed to settle several hours after cooling. The clear supernatant liquid was then decanted and the residue further separated from the mother liquor by washing in a bottle centrifuge. The sludge recovered was then electrodialyzed several days.

The soil residue after the sulphur-dioxide treatment was washed several times with small quantities of water and the washings included with the material described above. The soil residue was then extracted with 2 percent ammonia, and the extraction continued until 8 to 10 liters of clear filtrate were obtained. The washings were very dark at first, but the color was greatly diminished at the end of the

washing. There is no definite end point to such washing. However, very little residue was obtained from the evaporation of the last portions of the leachings. The whole of this filtrate was evaporated to dryness before being subjected to electrodialysis.

A second set of extractions was made in the same manner as the first except in reverse order; that is, extraction was made first with 2 percent ammonia followed by sulphurous acid. The filtrates were treated as described above.

The three soils used in this investigation included the B₂ horizon of the Becket loam from Massachusetts. This is a typical podzol having no hardpan but a large accumulation of organic matter in this layer. This profile was described in detail in a previous publication (4).

The Trenary fine sandy loam from Alger County, Mich., is also a typical podzol. The B horizon which was used formed an indurated hardpan. Complete chemical data for this profile have not yet been published by this division.

The other sample was the surface horizon of Carrington loam from Buchanan County, Iowa. This is a typical prairie soil.

CHEMICAL CHARACTER OF EXTRACTED MATERIALS

Some of the fractions were small and only a limited number of chemical determinations could be made with the material available. However, so far as possible, the following determinations were made: Hydrogen-ion concentration, ash, ammonia absorption, total carbon, sulphur, and nitrogen, and, in two cases, hydrogen was also determined.

The carbon content of the soil residues, after the various extractions, are given in table 13, and the chemical data for the various extracts in table 14.

TABLE 13.—Carbon content of soils and soil residues

Soil	Treatment	Carbon content of soil and residue	Part of original carbon removed
		Percent	Percent
Becket loam, B ₂ horizon.	Untreated.....	2.61
	Extracted with NH ₄ OH only.....	1.00	61.7
	Extracted with SO ₂ followed by NH ₄ OH.....	.50	80.8
	Extracted with NH ₄ OH followed by SO ₂69	77.4
	Extracted with SO ₂ only.....	1.06	69.4
Carrington loam, A horizon.	Untreated.....	3.21
	Extracted with NH ₄ OH only.....	2.54	11.5
	Extracted with SO ₂ followed by NH ₄ OH.....	1.53	52.3
	Extracted with NH ₄ OH followed by SO ₂	2.43	24.3
	Extracted with SO ₂ only.....	2.21	31.2
Trenary fine sandy loam, B horizon.	Untreated.....	1.04
	Extracted with NH ₄ OH only.....	.52	68.3
	Extracted with SO ₂ followed by NH ₄ OH.....	.42	74.4
	Extracted with NH ₄ OH followed by SO ₂59	64.0
	Extracted with SO ₂ only.....	.88	46.3

¹ Calculations are not corrected for the small change in sample weight due to the part removed by extraction.

TABLE 14.—Organic fractions extracted from soils by SO_2 and by NH_4OH

Soil	Treatment	pH after electro-dialysis	Ash	Part of whole soil	Ammonia absorbed per gram of material	Total carbon	Carbon on ash-free basis	Total hydrogen	SO_2
		pH	Percent	Percent	Milliequivalents	Percent	Percent	Percent	Percent
Becket loam, B ₂ horizon.	Extracted with NH_4OH only	3.2	21.48	4.8	1.867	35.46	45.16	4.04	0.59
	Extracted with SO_2 after NH_4OH	N.D.	42.64	6	1.253	18.82	32.81	3.00	5.21
	Extracted with SO_2 only	4.0	17.55	2.8	2.765	35.63	43.27	3.34	2.88
	Extracted with NH_4OH after SO_2	2.8	10.85	1.6	2.478	43.10	48.01	4.45	2.00
Carrington loam, A horizon.	Extracted with HCl		31.30		2.870	40.20	58.06	3.45	
	Extracted with NH_4OH only	2.9	16.43	1.1	2.212	37.19	44.50		1.10
	Extracted with SO_2 after NH_4OH	7.0	23.81	1.1	.815	37.67	49.31		5.28
	Extracted with SO_2 only	5.3	53.17	1.3	.750	11.10	23.83		4.15
Trenary and sandy loam, B horizon.	Extracted with NH_4OH after SO_2	2.9	14.40	1.0		28.22	32.97		1.93
	Extracted with NH_4OH only	2.7	24.87	3.1	2.650	33.47	44.55	3.19	.74
	Extracted with SO_2 after NH_4OH	5.2	57.90	1.0	1.210	13.00	30.88	3.60	6.47
	Extracted with SO_2 only		30.01	2.8	2.318	25.63	38.65	3.01	4.55
	Extracted with NH_4OH after SO_2		26.90	2.3		33.91	46.39	3.08	3.41

¹Analyses by Joseph R. Spies, Insecticide Division, Bureau of Chemistry and Soils.

Large quantities of organic matter were extracted from each soil by sulphur-dioxide solution and by ammonia. The behavior of the two classes of soils was distinctly different with respect to the two solvents. Taking the reduction of carbon content of the soil residues as a measure of the amount of organic matter removed, interesting comparisons may be made.

In the case of the podzol soils about the same amount of organic matter was extracted by sulphur dioxide as by ammonia, about 60 percent of the total in each case. The organic matter of the Carrington soil reacted toward the solvents in a very different manner. Ammonia alone removed only about 12 percent of the carbon, while sulphur dioxide alone took out over 30 percent. In each case these values are very much lower than for comparable treatments of the Becket soil and distinctly lower than those of the Trenary soil. It is not surprising that the organic matter of the Carrington soil should be of relatively low solubility in ammonia on account of the fact that it is nearly neutral soil, presumably containing much of the organic matter in the form of calcium humate while the Becket, as well as podzols in general, contains strongly acid humus. The marked increase in the amount of organic matter removed by ammonia when this treatment was preceded by extraction with sulphur dioxide in the case of the Carrington soil is further evidence of the influence of bases upon the solution of humus by ammonia. Aside from differences which undoubtedly exist in the base content there is evidence of greater solubility of the organic fraction of the Becket soil than of the Carrington. The evidence of difference is indicated by the soil residues as well as by the extracted organic fractions as shown in table 13.

It should be pointed out that these fractions obtained by extraction are not sharply defined. It is not practical to continue extraction with sulphurous acid until no color is imparted to the solution and no precipitate obtained on boiling. The indefinite line of demarcation between the soluble and the insoluble organic matter by this

solvent is further complicated by the very considerable amount of sesquioxides brought into solution after long extraction. The quantities of these are such as to make the ash content of the extracted material too high to be of much value for satisfactory organic studies.⁵ Extraction with ammonia is also a time-consuming process if continued until a dark color disappears. In either case judgment must be used, and the results given are for materials extracted in a manner as nearly comparable as seemed practical to undertake.

The organic fractions studied do not, of course, contain all of the material extracted from the soil, for a part of it was lost by solution in the processes of dialysis and electrodialysis, and the part extracted by sulphur dioxide and not precipitated by boiling is not included. It seems highly probable also that a part of the material extractable by sulphur dioxide would also be extractable by ammonium hydroxide if not previously removed. Likewise, a part of that removed by ammonia would, if present in the soil, have been removed by sulphur dioxide.

The organic material extracted by hydrochloric acid from Becket loam has a much higher carbon content, calculated on an ash-free basis, than any of the other organic fractions. The value of 58.6 percent is much higher than the mean of values obtained in these experiments and elsewhere but is still considerably below the maximum reported for soil organic matter and is well within the range of values which might be expected from carbonaceous compounds without suspicion of the presence of charcoal. The presence of the latter was of course practically excluded in these cases by the fact that the extracts were all passed through Pasteur-Chamberland filters. Furthermore, the carbon content is almost identical with the carbon content of the theoretical compound suggested by Odén as the principal constituent of humic acid (26).

AMMONIUM HYDROXIDE EXTRACT

The organic colloids extracted by ammonia from each of the three soils show remarkable similarity in carbon content; in fact, the carbon contents calculated on an ash-free basis are practically identical. The values lie within the range of carbon contents given by Cameron and Breazeale (9) for extracted humus. It is not surprising that the ammonia extracts have a fair degree of constancy of composition. This material includes the so-called humic acids, concerning which so much has been written. While these acids are generally assumed to be made up of more than one compound they are, for the most part, regarded as consisting of closely related compounds. Perhaps more information is available concerning this group of compounds than any of the other soil organic material. Presumably the so-called humus nucleus described by Waksman (36, 37) would be included in this material.

SULPHUROUS ACID EXTRACT

The material extracted by sulphur dioxide presents some striking contrasts with that obtained by ammonium hydroxide. The fractions are in each case of distinctly lower carbon content than the

⁵ The ash content could no doubt be greatly lowered if this material were further fractionated by solution in alkali and reprecipitation by hydrochloric acid in accordance with conventional procedure for the preparation of humus. For the present, however, it was not considered desirable to subject the material to these additional transformations.

materials extracted by ammonia from the corresponding soils. This difference is least pronounced in the Becket and most pronounced in the Carrington. The fact that the two soils are different in this respect is not particularly surprising in view of the difference in the location of the organic matter with respect to horizons. In the B horizon of the podzols the bulk of the organic matter has undoubtedly been transported there from the overlying material. The probable mechanism of this shifting has been previously discussed (p. 19). In this shifting there appears to have been considerable selection of material—that is, a partial fractionation tending in the direction of uniformity of transferred material. Although the carbon content of this transferred material tends in the direction of uniformity, very considerable differences in the different fractions occur. In the Carrington surface soil, where fractionation has presumably been but little operative under natural conditions, most striking differences in composition by laboratory fractionation are shown.

Read and Ridgell (32) found a mean value of 49.26 percent for the carbon content of a large group of soils, while their corresponding subsoils had a mean value of only 39.16 percent carbon. This fractionation which gives rise to differences in carbon content doubtless leads also to the differences in carbon-nitrogen ratio which are often found in most soil profiles. (18)

Extraction with hydrochloric acid, as well as with bases, indicates that a portion of the soil organic matter is of amphoteric character. Therefore, sulphurous acid might be expected to effect solution because of its hydrogen-ion concentration and because this material is soluble in acids. Sulphurous acid might then be expected to react in a similar manner. On the other hand, sulphurous acid offers opportunity for reactions aside from the ordinary amphoteric behavior. If the soil organic material consists largely of lignin, or of compounds closely related to lignin, as certain information indicates (19, 25), it seems probable that reactions of the type occurring between wood and calcium sulphite might result. There is some evidence that such is the case.

Qualitative observations on the behavior of the material extracted by sulphur dioxide indicated the presence of sulphur in a form different from that of simple sulphites or sulphates, both of which were probably also present. In the process of electrodialysis simple salts, even those of fairly low solubility, are usually removed in 3 to 4 days. The materials extracted by sulphur dioxide behaved very differently, however. The titrable bases were removable in a normal manner but the anions were not. After several days very appreciable quantities of sulphates continued to pass into the anode chamber. When electrodialysis was continued for a period of 8 days with one sample the quantities passing through the membrane were still appreciable, indicating no practical end to this process.

The sulphur contents of the different fractions where sulphur dioxide was involved were much higher than those extracted by ammonia. The variations between the different samples are not capable of any very definite interpretation in view of their indefinite behavior on electrodialysis. They show, however, a marked tendency of the organic matter to combine with sulphurous acid.

If the organic substance is of the nature of lignin (or of a wide variety of other substances for that matter) the most probable

type of compounds formed would seem to be the sulphonic acids. This type of acid should be saponified by calcium hydroxide and the sulphur present in the form of sulphonic acids be converted to sulphate, which would be more readily electrodialyzable.

A sample of the fraction extracted by sulphur dioxide from the Becket soil was adjusted to about pH 7 with calcium hydroxide, boiled, and allowed to stand several hours, then filtered, washed, and electrodialyzed. Calcium and sulphate ions were both rapidly removed. After 24 hours no further trace of sulphate was obtained on further electrodialysis. A sample of the material analyzed for sulphur at this point showed a reduction in sulphur-trioxide content from 2.88 percent at the beginning to 1.72 percent. More complete data are shown in table 15. This compound was further treated by adding calcium hydroxide until the solution, after approximate equilibrium was established, was distinctly alkaline to phenolphthalein. After boiling and subsequent electrodialysis no appreciable sulphate was found in the anode chamber and the sulphur content of the electrodialyzed material was now 1.71 percent sulphur trioxide, or identical within the limits of analytical error with that produced by one alkaline treatment. The resulting compound was still of much higher sulphur content than the organic portion of the colloid as a whole extracted from this soil profile and described in a previous bulletin (4). There is some indication, therefore, that sulphur dioxide is instrumental in fixing a small amount of sulphur in the organic matter in a stable form. This is, in some respects, similar to those compounds reported by Feustel⁶ as being formed between peat and ammonia under pressure, in which the nitrogen is no longer in the form of an ammonium compound. The data at hand offer no conclusive evidence regarding the chemical character of the material. Indications point toward the frequently made assumption that lignin plays an important part in this respect. Steps are being taken to obtain further evidence on this point by determination of the methoxyl group, which is so characteristic of lignin from different sources.

TABLE 15.—Ammonia absorption and SO_2 content of organic soil fractions before and after treatment with $Ca(OH)_2$ *

Kind of soil	Reagent used for extraction	Ammonia absorbed per gram of material		SO_2 content	
		After electrodialysis only	After $Ca(OH)_2$ treatment and subsequent electrodialysis	After electrodialysis only	After treatment with $Ca(OH)_2$ and subsequent electrodialysis
		<i>Milli-equivalents</i>	<i>Milli-equivalents</i>	<i>Percent</i>	<i>Percent</i>
Becket loam, B ₁ horizon.....	SO_2 solution.....	2.76	2.01	2.88	1.71
Trenary fine sandy loam, B horizon.....	do.....	2.32	2.11	4.65	1.87
Orrington loam, A horizon.....	do.....	.75	.65	4.15	2.04

* Each of these samples is a subsample of the fraction extracted from soil by SO_2 solution and electrodialyzed. (See table 13.)

* Unpublished data.

In order to test the behavior of a purified lignin by the reagents used in these experiments a sample of corn-cob lignin furnished by Max Phillips, of the Farm Waste Division of this Bureau, was treated with sulphur-dioxide solution and the extract boiled until reduced to about one third of its volume. No precipitate was formed but some brown coloration was present. Evaporation of the solution to dryness showed 7.6 percent of the sample weight dissolved. It is evident that this kind of lignin was not present in the soil fraction recovered by boiling the sulphur-dioxide solutions of the soils. It appears also that the sulphur dioxide possesses a very different solvent power for lignin from that shown by the sulphite cooking liquor used in the paper industry. This behavior tends to obscure the part played by the solvent action due to sulphonation and that arising merely from the hydrogen-ion concentration of the sulphurous acid and its action as an acid upon the amphoteric organic material.

The hydrogen-ion concentration determinations of the different colloids were made on suspensions of the material in which a considerable amount of solids was present. No great significance should be attached to small differences in pH values, since concentration of solid material and state of dispersion have so much to do with the values obtained in these determinations.

General relationships stand out as significant, however. The group of acids extracted by ammonia show the greatest hydrogen-ion concentrations when in suspension. This is in line with the assumption of relative simplicity for those acids forming readily soluble salts. The material extracted by sulphur dioxide is much less acid, sometimes approaching neutrality. This is probably due in part to the character of the inorganic portion which appears to be largely alumina, the pH value of which when pure is approximately 8. Its reaction with the organic acids has doubtless left a mixture of organic acids and salts. The organic acids aside from their inorganic base content are doubtless less acid than the so-called humic acids, and a part of the hydrogen-ion concentration measured may have been due to the presence of sulphur in a sulphonic acid derivative. Even after saponification and removal of what appears to be sulphonic acids the material is still acid.

The range of pH values of the material extracted by sulphurous acid is comparable with the isoelectric pH values of some of the typical amphoteric organic compounds such as certain proteins. Casein for example has an isoelectric pH value of 4.6. This is about the value attained on electrodialysis, and a determination of its ammonia-holding power by the methods used here showed a value of 0.38 milliequivalent per gram or somewhat below that of the lowest values for fractions of the soil organic matter.

The acid properties of the organic fractions are further evidenced by ammonia-absorption capacity. This is shown in table 14.

There is much irregularity among the ammonia-absorption values. The materials extracted by ammonia from different soils are not greatly different. Those extracted by sulphur dioxide are widely different. This is no doubt due in part to the variable sulphur content but this factor is probably not as important as that of the organic composition aside from the sulphur compounds. Even with the sulphur present the ammonia absorption of the materials extracted from the Carrington soil with sulphur dioxide is very low. The low value appears not to

be due to the magnitude of dilution by the ash content alone, although the reaction between the ash material and the organic matter may be the most significant factor. Table 15 indicates that while the sulphur content of the colloids has an influence upon ammonia absorption, the magnitude of this influence is not more than about 25 percent of the total in any of the cases tested.

FUNDAMENTAL VARIATIONS IN SOIL ORGANIC MATTER

In the earlier studies of soil colloids in general many determinations were made which were of value in characterizing certain soils. Experience proved, however, that some of these methods were not of general value in indicating fundamental similarities and differences in the great groups of soils, hence many of such methods have had only limited use and have been largely discontinued since this branch of soil science has taken a more systematic form. Certain determinations, however, appear to be of a more fundamental character and their use has been of great value in the organization of systematic study of inorganic soil colloids. Systematic study of organic colloids has been much less developed. It is hoped, however, that further experience may show that some of the determinations herein described possess merit as a basis for systematic study and that the indications of similarity and difference in the organic matter of the few soils studied may prove to be of general application. A part of these methods appear to merit further study, at least in their application to the organic matter of profile samples of the soils of the great soil groups. The features which are particularly promising are those of a comparison of the organic matter extracted by sulphur dioxide solution with that extracted by ammonia from debased soils. The carbon and ash contents of these fractions and their base-exchange capacity by ammonia appear to possess the greatest diagnostic value. The base-exchange capacity when determined on material extracted by sulphur dioxide is probably of more value after treatment of the sample with calcium hydroxide to remove the loosely held sulphur compounds. Preparations are now under way to extend this work to samples from the great soil group and thus further an attempt to accumulate systematic data by which to relate the character of soil organic matter to existing schemes of soil classification.

SUMMARY

A study of the organic matter of soils from the colloidal standpoint is presented.

Dispersed organic colloids prepared from various soil-forming materials were studied by methods similar to those used in the study of inorganic soil colloids. The materials included rotted hay and straw, leaf mold, bacteria, and fungous bodies, and soil materials from peats and from other soil sources.

The various colloids contain ether, alcohol, and water-soluble components and in most cases significant quantities of cellulose and hemicellulose. The largest single component is the ligno-humic complex which varies between wide limits.

The electrodyalyzed colloids are strongly acid, the pH values of the viscous material ranging between 2.3 and 3.7.

In terms of milliequivalents the quantity of sodium hydroxide required to neutralize these colloids is considerably less than the quantity of ammonia taken up from dilute ammonium hydroxide.

The water-vapor absorption of the organic colloids over 30 percent sulphuric acid is as high or higher than the values for the most active inorganic soil colloids. In general, the properties of these organic colloids suggest the presence of either these or similar compounds in the soil.

Organic colloids, when mixed with quartz flour, show a moderate decrease in ammonia-absorbing power. When mixed with Cecil soil colloid the decrease in absorption is much greater, indicating the probability of chemical reaction between the acid organic colloid and the sesquioxides of the soil colloid.

The acid qualities of organic colloids are not much diminished by mixing with ferric hydroxide, are much more diminished by mixing with aluminum hydroxide, and are almost, if not entirely neutralized by mixing with ferrous hydroxide. These facts are utilized in the interpretation of certain soil profile characteristics.

From certain soils considerable organic matter may be dissolved by the action of acids in moderate concentration. There is evidence that much of the organic matter thus dissolved is in the form of organic cations.

The amphoteric character of soil organic matter was utilized in its separation into major fractions from three different soils by the use of hydrochloric acid, sulphurous acid, and by ammonia. The fractions extracted by ammonia are nearly uniform in carbon content, but show moderate variation in other characteristics. Materials extracted by sulphur-dioxide solution show wide variations in carbon content, in ammonia absorption, and in other ways. There is evidence that the character of fractions extracted by this reagent may be of diagnostic value in the study of soil profiles.

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