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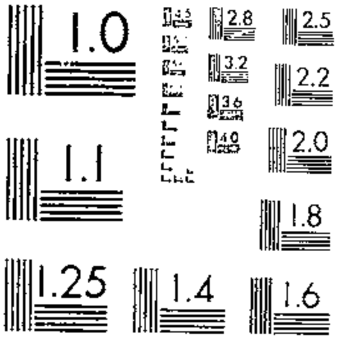

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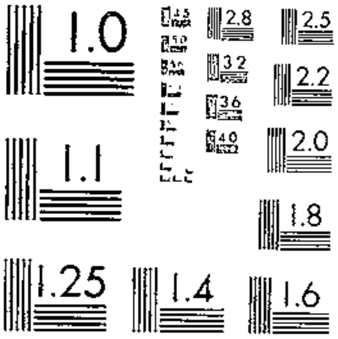

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NEUTRALIZATION CURVES OF THE COLLOIDS OF SOILS REPRESENTATIVE OF THE GREAT SOIL GROUPS

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INTRODUCTION

For a number of years the Bureau of Chemistry and Soils, as well as other institutions, has been engaged in a study of the fundamental character of soil colloids (*5, 14*).[1] The Soil Chemistry and Physics Research Division has been particularly interested in a study of the relationship between the chemical character of soil colloids and soil morphology (*3, 18, 19, 30*). In carrying out these investigations, recognized procedures employed in fundamental chemical and physical research have been adapted to the particular problems at hand. One of the tools of the physical chemist, widely used in the study of acids in general, is the neutralization, or titration, curve. The value of such data in connection with soil colloids has been emphasized by Bradfield (*10*), Baver (*7, 8, 9*), Scarseth (*51*), Puri (*47*), and others. Widely differing results have been obtained.

The character of the acids of soil colloids is of great importance scientifically because these acids are progressively transformed through natural agencies from their origin in the decomposing rocks to their end in nearly inert materials, such as the Laterites, or into soluble materials which are leached out. Agriculturally, the acids are important because in their youth they control the nutrient bases held, later they influence the capacity of soils to take up and hold lime and fertilizer bases, and finally, as they become still weaker

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[1] Italic numbers in parentheses refer to Literature Cited, p. 35.

and more admixed with sesquioxides, they have a markedly detrimental influence upon soil fertility through their fixation of phosphate and other ions added with fertilizers (*27*).

Titration curves offer an additional avenue of approach to further information regarding the acid and amphoteric behavior of the colloids. Characteristics which have made the colloids resistant to change by natural processes, however, greatly complicate the interpretation of what would often appear to be relatively simple data. That is, in any such studies, it must be borne in mind that we are dealing with substances which are for the most part amphoteric and essentially insoluble, with their acid salts, or, in some cases, with the acids themselves. The highly immobile anion is capable of only very slow diffusion, and the micelles possess the properties of semipermeable membranes, through which membranes a considerable part of the bases are not readily moved. In spite of the obstacles presented by the nature of the material, however, it is felt that much valuable information may be obtained from the acid-base relationships. Particularly important is the fact that titration curves express base-exchange capacity over a broad range of pH values.

Almost as soon as suitable methods of measuring the hydrogen-ion concentration of soils had become known, investigations were reported regarding the buffer action of soils to both acids and alkalies. Some of these data are presented in the form of titration curves; in other cases the data, although adequate for expression in this form, are given in tabular form. In most cases the starting point is the unaltered soils of varying pH values and varying degrees of saturation. In most cases the mechanical composition of the soil is not known except as roughly expressed by its textural classification. Interpretations of soil-titration curves in terms of their colloids are usually very unsatisfactory, both on account of omission of information regarding the quantity of colloid present and lack of knowledge of the character of the noncolloidal material, or, indeed, of the colloid itself.

It seemed, therefore, of considerable importance to attack the problem through the use of electrodialyzed colloids, in order to relate differences in colloid character as shown by titration curves to the soil-classification system and to the composition of the soil colloids. The minimum pH values of electrodialized soil colloids vary with the chemical character of soil colloids (*3*). Such data are also included. For purposes of this investigation, colloids are used which were obtained from typical profiles from the great soil groups. The chemical and mechanical composition of each of the soils and the chemical composition of the colloids are known.

Titration curves for the buffer action of whole soils are sometimes in general agreement. However, this is by no means always the case. The lack of concordant results by different investigators is probably due in part to variations in procedure and in part to the widely differing character of the soils studied. From reports covering a considerable number of investigations, certain generalizations regarding the more important features of the work may be made. Regarding the influence of colloidal material upon the buffer capacity of soil, the work of Kuchinskii (*36*) appears to express fairly general experience. He states that the illuviated horizons have the highest buffer capacities and eluviated horizons the lowest. When clay particles are removed from soil, the buffer capacity of the residue is practically zero. On the other hand, Myers and Gilligan (*43*) feel that such a general statement is not tenable. The buffer capacity of organic matter is ordinarily very high, much higher than for clays (*6*, *20*, *21*, *29*).

The reaction of any kind of alkali with a soil takes place much more slowly than ordinary reactions between substances entirely in solution. Results vary somewhat, but, in general, it appears that from 6 to 72 hours are necessary to reach an approximate equilibrium. The time required increases as the systems become more alkaline; 24 or 48 hours are time periods frequently used (*50*, *56*, *57*, *58*).

The time required to reach a constant pH value is considerably shortened when some soluble neutral salt is present, but the presence of the neutral salt produces a system distinctly more acid than when equal quantities of alkali solution alone are added (*1*, *24*).

Soil-titration curves vary widely (*35*, *55*, *57*). Some investigators have found fairly definite breaks in the curves at or near pH 7 (*6*, *25*, *32*, *44*), while others have found breaks at widely varying pH values or in many instances no significant breaks at any pH (*21*, *49*, *52*).

Much of the literature dealing with titration curves of whole soils is not readily applicable to the studies reported here, but the references cited above, together with a few others (*38*, *53*, *61*), are of definite significance as pointing to the results which may be expected from soil colloids taken alone (*12*, *42*, *51*).

EXPERIMENTAL PROCEDURE

In view of the fact that the reaction between inorganic soil colloids and alkalies is slow and that considerable time must be allowed for each increment of base to react before pH determinations are made, the method used in making soil-titration curves is necessarily arbitrary in several respects. Some variations in results should be expected from changes in technique. It is thought, however, that this procedure, when all things are considered, is well suited to the problem at hand.

The colloids were extracted from the soils by the use of a supercentrifuge and without the use of a dispersing agent, with a few exceptions, which are indicated later. The samples were concentrated and air-dried in a conventional manner, then ground to pass a 50-mesh sieve. The pulverized colloid was added to water and electrodialyzed, using an improved Mattson-type cell (*39*). When electrodialysis was complete, the colloid was dried on a slow steam bath and again ground to pass a 50-mesh sieve. In a previous investigation a colloid suspension, standardized as to weight, was used (*4*). Material in a state of suspension is in some respects more desirable for purposes of electrodialysis and subsequent titration than is the air-dried product. However, certain disadvantages made suspensions unsuitable for use in the present investigation. On long standing, suspensions may undergo certain alteration, particularly when organic matter is present. Furthermore, many of the samples used were subsamples of materials previously analyzed and reported. These samples had been preserved in an air-dry condition.

Samples of material to be tested were weighed and placed in 60-cc Erlenmeyer flasks. The quantity used in each flask was ordinarily the equivalent of 1 g oven-dry weight, but this varied in special cases, particularly if the material in a dilution of 1 to 10 formed a mass with inconveniently high viscosity. Varying quantities of boiled distilled water were added, the final volume in each case being about 10 cc.

To the first flask was added water only. To the second, 9 cc of water and 1 cc of a 0.1 N solution of sodium hydroxide were added, to the third, 2 cc of alkali, and so on until the alkali was sufficient to bring the suspension to at least a pH of 10. When more than 10 cc of 0.1 N sodium hydroxide was required, a more concentrated solution was substituted. If less than 1 cc of alkali is required, a solution more dilute than 0.1 N is preferable. The number of samples necessary to establish a suitable number of points varies with the character of the material. Ordinarily about 10 are sufficient. The samples were tightly stoppered and shaken at intervals for a period of 36 to 48 hours. A part of the suspension was then transferred to an electrode vessel and the hydrogen-ion concentration determined.

The earlier determinations of this investigation were all made with a hydrogen electrode, using a bubbling-type electrode vessel. During the progress of the work a glass electrode set-up was completed, which was found to be much more satisfactory in certain cases, particularly where the manganese content of the material was high. In many cases, none of which is indicated, the samples were run by both methods. Unless some interfering factors were operative the results by the two methods usually agreed within 0.2 pH. Many, but not all, determinations were made in duplicate. Agreement of duplicates varied with the character of the colloid, but in most cases the variation was not greater than 0.2 pH.

The results are expressed graphically by plotting the milliequivalents of sodium hydroxide per gram of material as abscissas and pH values as ordinates.

If the first series of determinations did not carry the pH values to 10 or higher, or if the initial concentration of sodium hydroxide markedly increased the pH, a second set was run, using greater or less quantities of alkali, as the case required. Furthermore, if definite breaks in the curve were not shown, but the possibility of such was indicated, additional samples were run, using smaller increments of alkali over a particular range to determine whether or not such breaks occurred.

In some cases where the organic matter was high, the bulk of it was removed by treatment with hydrogen peroxide in a conventional manner (*45*). This treatment, when used, is indicated in the legend of the graph. There is some question as to whether a minor alteration of the properties of the inorganic colloid takes place on this treatment. Several tests indicate that the effect, if any, is negligible unless alkali or a considerable amount of some other electrolyte is present, in which case alteration may be appreciable.

DESCRIPTION OF SOILS

In most cases the soils used in this investigation have been or will be described in other publications of this Bureau. Only brief descriptions covering the most pertinent information are given here of samples, the full descriptions of which appear elsewhere. Each profile, with the exception of the Caribou, was collected by some member of the Soil Survey Division, and is representative of the great soil group indicated.

The terminology for designating vertical sections of soils is that used by the Soil Survey Division. When, in the judgment of the collector, the morphological relationships justify the terminology A, B, and C for the horizons, these are used. However, sometimes, particularly in Pedocal soils, the morphological relationships are not readily distinguishable. In such cases vertical sections are numbered from the surface downward.

Some of the profiles, particularly certain of the Podzols, were collected several years ago. Since that time the nomenclature for horizons has become more explicit. Profiles previously studied do not in all cases have horizon designations in conformity with the rules which from now on will be uniformly applied.

Pedocal soils are represented by a Desert profile and by a Chernozem. The Desert soil is a profile of the Pima clay adobe, 2 miles from the college farm near Mesilla Park, N. Mex. (*15*). The area is unirrigated virgin soil. The horizons are based primarily on textural differences.

Horizon 1, 0 to 9 inches. Clay adobe, dark brown.
Horizon 2, 9 to 29 inches. Clay adobe, dark brown.
Horizon, 3.29 to 41 inches. Silty clay, lighter than the layer above.
Horizon 4, 41 to 45 inches. Clay very much like surface.

The Chernozem profile is Hastings silt loam from Sherman County, Nebr. The annual rainfall of this section is about 25 inches (*16*).

The Carrington profile is from Buchanan County, Iowa, and is typical of Prairie soils (*18*). The annual rainfall of this section is about 33 inches. This profile was collected 1 mile southwest of Winthrop. The area had not been cultivated. The description follows:

Horizon A_1, 0 to 3 inches. This material is a very dark grayish-brown loose mellow granular loam, and contains much silt. It forms a turf loosely held by grass roots.
Horizon A_2, 3 to 13 inches. A very dark grayish-brown fine granular loam.
Horizon B_1, 13 to 22 inches. This is a transition layer ranging in color from very dark in the upper portion to brown in the lower. It represents the transition from the surface soil to the subsoil. It is imperfectly granular in the upper portion and structureless in the lower.
Horizon B_2, 22 to 43 inches. This is a brown loam, slightly heavier in texture than the layers above. There is no carbonate present.
Horizon B_3, 43 to 70 inches. Brown clay loam splotched with yellow and rusty brown, streaked by occasional dark tongues. A few boulders and gravel are present. This is the partly decomposed parent drift, leached of its carbonates.

The Miami profile is characteristic of the Gray-Brown Podzolic group as it occurs west of the Appalachian region. The sample used was taken in a virgin area in Grant County, Ind. (*18*).

Horizon A_1, about 1½ inches thick. A very dark brownish-gray silt loam high in organic matter.
Horizon A_2, 1½ to 9 inches.
Horizon B, 11½ to 23½ inches. It is a heavy brown plastic silty clay.
Horizon C, 27 to 48 inches. Consists of rather hard medium-textured calcareous till of late Wisconsin age.

The Muskingum soil is another example of the Gray-Brown Podzolic group, but shows less evidence of maturity than the Miami series. The sample was taken near Zanesville, Ohio (*41*).

Horizon 1, 0 to 7 inches. Light grayish-brown to yellowish-brown silt loam.
Horizon 2, 8 to 13 inches. Yellow silty clay loam.
Horizon 3, 14 to 24 inches. Compact yellow silty clay, mottled with gray.
Horizon 4, 25 to 46 inches. Light reddish-yellow silty clay, slightly mottled with gray.
Horizon 5, 47 to 72 inches. Heavy dense gray clay.

The Ruston soils are Red lateritic soils of the coastal plains. The profile studied was taken near Cuthberg, Ga. (*18*).

Horizon A, 0 to 14 inches. Yellowish-red loamy sand.
Horizon B, 14 to 40 inches. Yellowish-red friable sandy clay.
Horizon C, collected to a depth of 60 inches. Mottled and streaked light-red, yellow, and grayish-yellow sandy clay material.

The Nacogdoches very fine sandy loam is a sample from the Red or lateritic soil group.[2] It was taken 16 miles east of Nacogdoches, Tex. A total of nine horizon samples were taken, but only four of them are included in this study. Some of them were closely similar in appearance and in chemical composition.

Horizon 1, 0 to 8 inches. Dark dull brownish-red fine sandy loam.
Horizon 4, 60 to 72 inches. Red and yellow mottled friable fine sandy loam.
Horizon 6, 108 to 132 inches. Reddish-yellow compact friable fine sandy loam.
Horizon 9, 180 to 372 inches. Dark green or greenish black, hardened compact made up of greensand marl.

Single horizons were used of a Columbiana soil from Costa Rica (*18*) and of an unnamed clay soil from Hawaii.

Three profiles of typical Podzol soils are included.

The Caribou loam profile was taken near Presque Isle, Maine (*18*).
Horizon A_1, 0 to ¾ inch. Composed of black pellets.
Horizon A_2, ¾ to 2 inches. A gray layer.
Horizon B_1, 2 to 4 inches. Has rich-brown color.
Horizon B_2, 4 to 6 inches. Bright yellowish brown. Heavier than the B_1.
Horizon C, 8 to 24 inches. Has a greenish blue-gray color and is composed of unweathered glacial drift.

The Au Train sand is a Podzol derived from almost pure sand (*18*). It was collected in Luce County, Mich. The horizons are described thus:

Horizon A_1, 0 to 2 inches. Leaf litter and mold.
Horizon A_2, 2 to 10 inches. Gray sand.
Horizon B_1, 10 to 12 inches. Very dark brown loamy sand.
Horizon B_2, 12 to 40 inches. Yellowish or reddish-brown sand.
Horizon C. Contained so little colloidal material that its extraction was impractical.

The Trenary sandy loam from Alger County, Mich., is an excellent example of a typical Podzol. The horizons are described as follows:

Horizon A_0, 0 to 2 inches. Leafmold.
Horizon A, 2 to 8 inches. Lavender-colored medium sand to loamy sand.
Horizon B, 8 to 20 inches. Light-brown or snuff-colored sandy loam. This is the ortstein but is only very slightly cemented.
Horizon C, 20 to 40 inches. A transition layer, mottled gray, yellow, and brown, slightly cemented to clayey sandy loam.
Horizon C_2, 40 to 60 inches. Yellowish-brown loamy sand, slightly cemented in places.
Horizon C_3, 5 feet +. Reddish to pinkish sandy clay. This is the parent material.

PREPARATION OF MATERIALS

Colloids were prepared from each of the soils according to the procedure generally used in this Bureau (*14*). A few were prepared

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[2] This Nacogdoches profile is closely similar to, but not identical with, the one referred to by Middleton, Slater, and Byers (*41*).

especially for this investigation; most of them were prepared in connection with other investigations, and their chemical compositions have been published in the various bulletins cited. Data for the Trenary profile have not been previously published. The mechanical analyses of the various horizon samples are given in table 1 and the chemical analyses in table 2. The chemical composition of each of the colloids used in this study is included in table 3. In each case the colloids were electrodialyzed to remove the exchangeable bases. The cathode dialysates were analyzed, and the anode dialysates analyzed for sulphates and phosphates. Analytical results of the dialysates are given in table 4. Electrodialysis is a very satisfactory method for preparing hydrogen-saturated soil colloids, but the cathode dialysates obtained are not altogether satisfactory for the analysis of exchangeable bases. The time required for dialysis varies for different colloids, and with some samples probably more of the bases, ordinarily nonexchangeable, are removed than is the case with other samples requiring less time. Furthermore, in most cases the membranes become impregnated with indefinite quantities of the insoluble bases, such as magnesium hydroxide, and with sesquioxides.

The relationship between the total quantity of each base constituent and the amount removed by electrodialysis is also given in table 4. These relationships are highly variable and are not greatly different in general from those previously observed (*5*). Specific cases will be discussed further in connection with the consideration of acid-base relationships of the various colloids.

TABLE 1.—*Mechanical analyses of Trenary fine sandy loam*[1]

Sample no.	Horizon	Depth	Fine gravel	Coarse sand	Medium sand	Fine sand	Very fine sand	Silt	Clay	Colloid <0.002 mm	Organic matter by H_2O_2	Mineral matter dissolved by H_2O_2
		Inches	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*	*Percent*
4580	A_0	1½–2	2.3	3.0	2.2	6.4	19.2	20.9	4.6	2.2	39.3	2.2
4581	A_1	2–8	.9	9.7	17.0	20.4	15.1	25.3	4.6	1.8	.9	.2
4582	B	8–24	1.5	9.8	17.1	31.7	13.3	15.4	7.5	5.2	3.3	.5
4583	C_1	24–40	2.0	13.1	15.9	31.5	11.6	14.6	7.9	6.3	.1	.2
4584	C_2	40–60	.4	20.1	29.0	36.6	5.8	2.9	4.9	3.2	.2	.2
4585	C_3	60+	.9	8.6	16.8	25.4	14.6	24.8	8.6	6.9	.1	.2

[1] Determinations by T. M. Shaw.

TABLE 2.—*Chemical analyses of Trenary fine sandy loam*

Sample no.	Horizon	Depth	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	SO_3	CO_2	N	Loss on ignition	Organic matter
		In.	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*	*Pct.*
4580	A_0	1½–2	44.90	4.95	1.05	0.14	1.13	0.23	1.91	0.51	0.20	0.10	0.20	(1)	1.10	44.92	40.10
4581	A_1	2–8	88.76	5.15	.89	.02	.28	.01	2.65	.48	.43	.02	.06	(1)	.05	1.32	1.07
4582	B	8–24	82.57	6.91	1.80	.04	.41	.10	2.84	.50	.34	.07	.07	(1)	.11	4.42	2.93
4583	C_1	24–40	87.21	6.47	1.12	.04	.10	.13	3.07	.48	.20	.05	.03	(1)	.01	.76	.26
4584	C_2	40–60	88.47	5.35	1.27	.03	.36	.27	2.50	.43	.23	.03	.01	(1)	.02	.87	.23
4585	C_3	60+	84.50	7.63	1.34	.03	.40	.44	3.25	.55	.32	.07	.04	(1)	.01	.90	.27

[1] None.

TABLE 3.—*Chemical composition of soil colloids used for neutralization curves*

Kind of colloid	Laboratory no.	Horizon	Depth	SiO_2	Al_2C_3	Fe_2O_3	MnO	CaO	MgO	K_2O	Na_2O	TiO_2	P_2O_5	SO_3	CO_2	Organic matter	Ignition loss	Molecular ratio	
																		$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	$\frac{SiO_2}{Al_2O_3}$
			Inches	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*		
PEDOCAL SOILS																			
Pima clay adobe	B706	1	0 – 9	51.79	21.42	7.04	0.08	3.06	4.05	2.52	(1)	0.55	0.21	0.06	0.90	1.25	8.91	3.43	4.10
	B707	2	9 – 29	51.58	20.24	7.78	.12	3.39	4.29	2.32	0.07	.53	.26	.07	1.35	1.12	9.39	3.47	4.32
	B708	3	29 – 41	52.40	19.64	8.08	.08	3.33	3.68	2.32	.32	.68	.38	.09	1.13	1.43	9.52	3.58	4.52
	B709	4	42 – 45	53.70	20.96	7.96	.07	2.11	3.48	2.46	.25	.66	.27	.05	.23	1.01	8.76	3.49	4.34
Hastings silt loam	8079	A_1	0 – 6	48.81	20.21	7.50	.09	1.09	2.37	1.77	.24	.71	.26	.26	.58	7.19	17.25	3.30	4.08
	8080	A_2	6 – 20	49.90	21.42	7.50	.09	1.02	2.33	2.24	.21	.61	.17	.31	.12	5.91	14.69	3.23	4.17
	8081	B_1	20 – 30	51.75	22.40	7.82	.07	1.04	2.61	2.26	.19	.62	.11	.20	.05	2.35	11.55	3.05	3.92
	8082	B_2	30 – 43	53.41	22.19	7.33	.06	1.21	2.87	2.04	.17	.66	.12	.16	.08	1.48	10.21	3.37	4.08
	8083	B_3	43 – 57	54.52	19.99	8.21	.07	2.00	3.18	2.15	.31	1.04	.25	.17	.34	1.02	8.95	3.66	4.62
	8084	B_4	57 – 78	55.10	19.51	8.18	.07	2.58	3.15	2.30	.26	.75	.23	.19	.25	.86	8.68	3.78	4.79
PRAIRIE SOILS																			
Carrington loam	10082	A_1	0 – 3	41.12	20.90	10.36	0.10	1.31	1.52	1.44	0.12	0.62	0.37	------	(2)	12.92	22.56	2.53	3.33
	10083	A_2	3 – 13	41.84	23.22	10.09	.14	.97	1.61	1.38	.04	.55	.36	------	(2)	9.94	20.18	2.39	3.06
	10084	B_1	13 – 22	43.82	24.34	10.67	.09	.94	1.71	1.31	.06	.68	.28	------	(2)	6.16	16.47	2.38	3.05
	10085	B_2	22 – 43	44.77	24.67	12.92	.08	1.02	1.71	1.63	.01	.82	.26	------	(2)	2.53	12.41	2.30	3.08
	10086	B_3	43 – 70	45.42	24.30	13.69	.07	1.14	1.81	1.85	.05	.87	.29	------	(2)	1.14	10.77	2.33	3.17
	10087	C	70 – 84	45.42	23.82	13.77	.08	1.48	1.79	1.89	.13	.82	.22	------	0.10	1.07	10.93	2.36	3.23
GRAY-BROWN SOILS																			
Miami silt loam	10341	A_1	0 – 1½	44.86	22.04	7.40	0.22	1.71	1.67	2.98	0.29	1.05	0.51	------	(2)	10.20	17.78	2.85	3.46
	10342	A_2	2½ – 9	47.46	22.98	7.94	.12	1.20	1.39	2.90	.22	.70	.40	0.22	(2)	6.82	14.90	2.87	3.51
	10343	B	11 – 24	47.07	23.38	11.[illegible]	.09	.96	2.09	4.37	.24	.67	.33	.12	(2)	1.68	9.45	2.60	3.42
	10344	C	28 – 48	46.13	22.97	10.[illegible]	.08	2.65	2.14	4.25	.22	.60	.37	.17	1.62	1.63	9.53	2.63	3.41
Muskingum silt loam	B407	1	0 – 7	44.00	26.67	9.97	.14	.93	1.98	2.51	.17	.62	.49	.09	(2)	3.94	13.18	2.26	2.80
	B408	2	7 – 13	43.10	27.26	13.00	.11	.95	1.90	2.78	.06	.72	.44	.05	(2)	1.25	10.00	2.06	2.68
	B409	3	14 – 24	42.70	29.79	11.13	.06	.65	1.54	3.25	.12	.73	.55	.02	(2)	.52	9.55	1.97	2.43
	B410	4	25 – 46	45.05	30.73	8.28	.05	.74	1.21	3.56	.09	.84	.60	.01	(2)	.30	9.08	2.12	2.49
	B411	5	47 – 72	46.80	31.30	5.26	.07	.82	1.62	4.26	.16	.92	.80	.02	(2)	.27	8.39	2.29	2.54

LATERITIC AND LATERITE SOILS

Ruston loamy sand	161	1	0 - 14	37.16	31.31	12.82	0.10	0.47	0.23	0.70	0.29	0.93	0.17	0.12	(2)	4.54	16.88	1.60	2.01
	162	2	14 - 40	36.60	32.58	12.70	.07	.44	.27	.70	.30	.99	.20	.10	(2)	2.56	15.37	1.53	1.92
	163	3	40 - 60	38.49	33.88	12.08	.04	.43	.28	.74	.28	.99	.16	.10	(2)	1.28	13.74	1.57	1.90
Nacogdoches very fine sandy loam	5028	1	0 - 8	32.17	23.88	28.05	.36	.51	.86	1.21	.27	------	.33	------	(2)	------	11.17	1.31	2.28
	5031	4	------------	33.50	22.39	29.20	.07	.35	1.26	1.10	.21	------	.28	------	(2)	------	11.16	1.26	2.53
	5033	6	108 -130	38.55	23.78	22.60	.08	.52	1.37	1.11	.22	------	.14	------	(2)	------	10.84	1.71	2.74
	5036	9	180+	33.43	15.20	33.13	(1)	3.18	4.54	.79	.33	------	.09	------	(2)	------	9.27	1.56	3.72
Columbiana clay	9804	A₁	0 - 10	22.04	36.02	15.36	.18	.33	.23	.18	.07	1.83	.48	------	(2)	6.44	24.11	.81	1.04
Clay soil from Kauai, Hawaii	B3719	3	16 - 33	12.65	23.74	38.41	.02	.44	.31	.25	.01	4.77	.42	.25	(2)	6.30	18.49	.44	.91

PODZOL SOILS

Au Train sand	10644	A₀	0 - 2	12.34	3.81	0.99	0.43	1.00	0.45	0.32	0.40	0.11	0.37	------	(2)	74.10	79.57	4.71	5.50
	10645	A₁	2 - 10	47.27	14.20	3.51	.07	.48	.57	.62	.50	------	.37	------	(2)	25.53	31.75	4.88	5.64
	10646	B₁	10 - 12	11.87	16.88	6.53	.09	.54	.33	.62	.22	------	.40	------	(2)	48.48	62.58	.88	1.19
	10647	B₂	12 - 40	12.38	23.96	4.70	.09	.42	.25	.48	.36	.27	.34	------	(2)	40.46	54.48	.78	.88
Caribou loam	10540	A₁	0 - ¾	34.57	16.90	5.26	.18	1.27	1.18	2.57	.21	1.15	.38	0.50	(2)	27.82	36.67	2.90	3.43
	10541	A₂	¾ - 2	43.31	21.84	4.82	.12	.72	1.33	2.62	.16	1.25	.57	.26	(2)	16.36	23.18	2.95	3.37
	10542	B₁	2 - 4	32.06	19.67	15.08	.08	.67	1.47	2.07	.06	.81	.65	.27	(2)	16.90	27.43	1.83	2.77
	10543	B₂	4 - 6	28.09	22.16	17.62	.05	.26	1.77	1.03	.33	.69	.42	.34	(2)	14.55	27.44	1.41	2.16
	10544	C	8 - 24	38.29	25.40	13.08	.18	.26	2.80	3.85	.09	.97	.32	.11	(2)	5.43	14.64	1.03	2.54
Trenary sandy loam	4580	A₀	1½ - 2	28.18	8.27	2.82	.12	1.01	.67	1.15	.19	.40	.29	.34	(2)	42.70	56.72	4.76	5.76
	4581	A₁	2 - 8	50.49	16.29	5.10	.06	.90	1.11	3.06	.22	1.30	.10	.26	(2)	14.68	21.32	4.87	5.26
	4582	B	8 - 24	28.42	19.44	9.65	.08	.62	1.21	2.22	.18	.99	.48	.26	(2)	21.22	36.46	1.89	2.47
	4583	C₁	24 - 40	49.79	23.48	8.30	.14	.61	2.42	5.30	.13	.86	.19	.09	(2)	1.87	8.54	2.87	3.59
	4584	C₂	40 - 60	42.91	24.09	8.46	.17	.31	1.82	3.90	.21	.79	.30	.12	(2)	7.80	16.88	2.46	3.01

MISCELLANEOUS NATURAL MATERIALS

Bentonite	154	----	----------	60.49	23.24	4.60	0.09	0.53	2.48	0.22	1.83	0.32	0.04	0.10	0.17	0.54	6.04	3.91	4.41
Halloysitic material	5690	----	----------	44.02	39.42	1.83	.10	(1)	.06	.05	(1)	.37	.03	.05	(2)	------	13.93	1.84	1.90

(1) Trace.

(2) None.

TABLE 4.—*Exchangeable and nonexchangeable monovalent and divalent bases in colloids* [1]

Sample	Depth	Ca			Mg			K			Na			Ca+Mg+K+Na		
		Total	Exchangeable	Part exchangeable	Total	Exchangeable	Part exchangeable	Total	Exchangeable	Part exchangeable	Total	Exchangeable	Part exchangeable	Total	Exchangeable	Part exchangeable
	Inches	*Milliequivalent*	*Milliequivalent*	*Percent*	*Milliequivalent*	*Milliequivalent*	*Percent*	*Milliequivalent*	*Milliequivalent*	*Percent*	*Milliequivalent*	*Milliequivalent*	*Percent*	*Milliequivalent*	*Milliequivalent*	*Percent*
PIMA CLAY ADOBE																
B706	0–9	1.093	0.971	89	2.009	0.184	9	0.535	0.049	9	(2)	(2)	--------	3.228	0.795	25
B707	9–29	1.211	1.221	100	2.128	.188	9	.493	.047	10	0.023	(2)	--------	3.241	.887	27
B708	29–41	.753	.725	96	1.726	.159	9	.522	.030	6	.080	0.029	36	2.977	.839	28
B709	41–45	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------	--------
HASTINGS SILT LOAM																
8079	0–6	0.389	0.246	63	1.175	0.124	11	0.376	0.057	15	0.077	(2)	--------	2.017	0.427	21
8080	6–20	.364	.339	93	1.155	.208	18	.475	.040	8	.068	0.035	51	2.062	.622	30
8081	20–30	.371	.332	89	1.295	.213	16	.480	.040	8	.061	.023	38	2.107	.608	29
8082	30–43	.432	.389	90	1.424	.238	17	.433	.044	10	.055	.010	18	2.344	.681	29
8083	43–57	.714	.536	75	1.577	--------	--------	.456	.044	10	.100	.029	29	--------	--------	--------
8084	57–78	.921	.464	50	1.066	.164	15	.488	.049	10	.084	.019	23	2.550	.696	27
CARRINGTON SILT LOAM																
10082	0–3	0.468	0.303	65	0.756	0.080	11	0.306	0.032	10	0.039	0.022	56	1.569	0.477	28
10083	3–13	.346	.221	64	.800	.114	14	.293	.021	7	.023	.007	54	1.452	.363	25
10084	13–22	.364	.264	73	.848	.059	7	.278	.018	6	.019	.013	68	1.502	.354	24

MIAMI SILT LOAM

10341	0- 1½	0.611	0.432	71	0.828	0.005	1	0.632	0.034	5	0.093	0.021	23	2.164	0.492	23
10342	2½- 9	.428	.361	84	.680	.005	1	.615	.010	2	.071	.019	27	1.803	.395	22
10343	11 -24	.343	.282	82	1.037	.050	5	.928	.025	3	.077	.003	4	2.385	.360	15
10344	28 -48	.946	.886	94	1.002	.070	7	.902	.030	3	.071	.035	49	2.254	.294	13

MUSKINGUM SILT LOAM

B407	0 - 7	0.332	0.082	25	0.982	0.050	5	0.533	0.010	2	0.056	0.023	41	1.900	0.165	9
B408	7 -13	.339	.132	39	.942	.035	4	.590	.021	4	.020	.006	30	1.891	.194	10
B409	14 -24	.232	.039	17	.764	.040	5	.690	.006	1	.039	.006	15	1.725	.091	5
B410	25 -46	.264	.046	17	.591	.045	8	.756	.006	1	.029	.003	10	1.640	.100	6

RUSTON LOAMY SAND

161	0 -14	0.168	0.043	26	0.115	0.005	4	0.062	0.011	18	0.093	0.003	3	0.438	0.062	14
162	14 -40	.154	.032	21	.135	(²)	--------	.077	.006	8	.116	.003	3	.484	.041	8
163	40 -60	.154	.021	14	.140	.005	4	.060	.011	18	.090	.003	3	.444	.040	9

AU TRAIN SAND

10644	0 - 2	0.571	0.489	86	0.225	0.080	30	0.068	0.015	22	0.129	0.029	22	0.993	0.613	62
10646	10 -12	.193	.136	70	.165	.010	6	.132	(²)	--------	.071	.019	27	.561	.165	29
10647	12 -40	.150	.143	95	.125	.005	4	.102	(²)	--------	.116	.023	20	.493	.171	35

TRENARY SANDY LOAM

4580	1½- 2	0.361	0.325	90	0.332	0.015	--------	0.244	0.015	6	0.061	0.048	79	0.998	0.403	40
4581	2 - 8	.321	.300	93	.551	.010	--------	.650	.019	3	.071	.058	82	1.593	.387	24
4582	8 -24	.221	.039	18	.600	.020	--------	.471	.011	2	.058	.045	78	1.350	.115	8
4583	24 -40	.218	.125	57	1.200	.010	--------	1.125	.021	2	.042	.035	83	2.585	.191	7
4584	40 -60	.111	.036	32	.903	.005	--------	.828	.017	2	.068	.039	57	1.910	.097	5

[1] When carbonates are present their calcium equivalent is deducted from the total and the exchangeable calcium content.

[2] Trace.

Where chemical analysis showed any considerable amount of organic matter, this was removed from a portion of the sample by hydrogen peroxide treatment in a conventional manner. Titrations were then made on electrodialyzed samples before and after the removal of organic matter.

TITRATION CURVES OF SPARINGLY SOLUBLE ACIDS

Before taking up the titration of the soil-colloid acids, it is well to consider the behavior of related substances which should be helpful in interpreting the soil data. The titration curve for phosphoric acid with its pronounced breaks corresponding to the neutralization of the primary and the secondary hydrogen atoms is one of the best-known examples of a curve showing polybasicity of an acid (*23, Ed. 2*). Certain other soluble, strong, polybasic acids, such as sulphuric acid, according to the work of Enklaar (*26*), show no perceptible break on neutralization of the primary hydrogen atom. In order to have data for comparison, titration curves were made of two polybasic acids, of definite composition and of very low solubility. Tungstic acid, H_2WO_4, and mucic acid, $(OH)_4C_4H_4(COOH)_2$, were selected. In each case commercial products were subjected to electrodialysis until practically free from bases. Titration curves were made in the usual manner, using 0.2 g of acid in each case instead of 1 g, as in the case of soil colloids. Most of the solids dissolved as the sample became alkaline.

Data for a group of other inorganic and organic substances definitely related to soil colloids are included for the purpose of comparison with the soil colloids. These are silicic acid gel,[3] aluminum hydroxide,[4] ferric hydroxide,[5] bentonite colloid, a colloidal product of halloysitic material,[6] and a synthetic silicate gel.[7]

The organic colloids used include humic acid extracted from the B horizon of Trenary soil, artificial humic acid prepared by the action of sulphuric acid on sucrose (*31*), and lignin prepared from corncobs.[8] A dilution curve was made by adding sodium hydroxide solution to water and treating in the same manner as when soil colloids were present.

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[3] Silicic acid was prepared by treating a solution of sodium silicate containing about 15 g of silica per liter with dilute hydrochloric acid. When distinctly acid it was allowed to stand overnight, then filtered by means of Pasteur-Chamberland filters and washed to reduce the salt content. It was then evaporated slowly to dryness, ground to a fine powder, again washed, and electrodialyzed. A more satisfactory product would be formed if it were never allowed to air-dry. However, the production of any considerable quantity of material of high purity in this manner involves an almost interminable process.

[4] Aluminum hydroxide was prepared by adding ammonium hydroxide to a solution of aluminum chloride. This was washed and electrodialyzed before being finally dried for use.

[5] Ferric hydroxide was prepared in a manner similar to that used for aluminum hydroxide. One sample was prepared, however, which was never allowed to dry. About 4 weeks of continuous electrodialysis were required to reduce the chloride content of the anode dialysates to a trace. This test was made after the current was passed through for a period of 24 hours. The material was then homogenized by drawing it through a finely perforated Gooch crucible. This concentration of the suspension was adjusted so that 20 cc contained about 1 g of dry ferric hydroxide.

[6] This colloid, isolated from a natural deposit, had a chemical composition corresponding very nearly to the formula $Al_2O_3.2SiO_2.2H_2O$ (*3*). An X-ray examination by S. B. Hendricks, of the Fertilizer Research Division, showed a crystalline structure similar to but not identical with a type specimen of halloysite.

[7] This gel was prepared by mixing together solutions of aluminum chloride, ferric chloride, and sodium silicate. The gel had been washed and dried, and was several years old when electrodialyzed for use. The silica-alumina ratio was 8.1, and the silica-sesquioxide ratio 5.8. An X-ray examination showed no crystalline structure.

[8] This sample of lignin was prepared by Max Phillips, of the Industrial Farm Products Research Division.

The titration data for the various colloids are presented in the form of point-to-point graphs rather than as smooth curves. Curves for the miscellaneous colloids described above are shown in figure 1 in three groups, each group having a scale adapted to the magnitude of alkali used and pH change.

The slightly soluble dibasic acids of definite chemical constitution each gave titration curves similar to those of relatively strong soluble monobasic acids with little or no evidence of their polybasic character. This serves to emphasize that the existence of polybasicity is not necessarily detectable from the character of a titration curve. On the other hand when two or more breaks occur their presence is strong evidence of polybasicity.

The dilution curve for sodium hydroxide is in general harmony with similar data presented by Bradfield (*11*). The new data are presented because details of procedure were identical with the procedure used when soil colloids were being titrated. For this reason they will be of value for comparative purposes later. The dilution curve shows pH values just a little lower than calculated theoretical values, which are not recorded here. The opportunities for carbonate formation readily account for this difference. The weak buffering effect of silicic acid in the slightly alkaline range and relatively strong buffering in the more strongly alkaline range is in harmony with previous work (*11*).

The curves for aluminum hydroxide and ferric hydroxide were not highly satisfactory when carried out in the manner used for soil colloids. They are so slightly buffered that in the pH range below about 10 small quantities of impurities have a marked influence upon pH values. It is very difficult to remove the last traces of diffusible anions from these gels, hence the possibility remains that some small part of the apparent buffering may have been due to the formation of sodium chloride. Several samples of material were prepared, and the results did not agree closely. However, an average was not taken, but the data for the sample thought to be purest are those recorded. The behavior of ferric hydroxide resembled that of aluminum hydroxide a little more closely than would be expected in view of the greater amphoteric character of the aluminum compound.

The important feature, so far as the present investigation is concerned, is brought out by the fact that hydrogen-ion concentrations of very dilute solutions of sodium hydroxide are but little changed by the presence of either aluminum hydroxide or ferric hydroxide, and that some other constituents of the soil colloids must be responsible for practically all their buffer effect. Considerable significance attaches to the behavior of alumina and ferric hydroxide, particularly the latter, because of the probability of their presence in the colloids of certain of the more highly leached soils.

The colloid of the halloysitic material, with its weakly acidic character,[9] stands in marked contrast to the strongly acidic character of the bentonite colloid.

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[9] Strength of acid is usually expressed in terms of degree of dissociation of material in solution. A more inclusive term is obviously desirable for expression of a comparison of the acid characteristics of colloidal or very slightly soluble acids. Clark (*23, Ed. 3*), in his treatise on hydrogen-ion concentration, calls attention to the fact "* * * there is no way to call forth the characteristic 'acid' properties of extremely weak acids except to attack *them* with bases * * *." In this bulletin acid character will be regarded as including not only the pH values of the colloidal acids, but also the hydrogen ions brought into activity on addition of a base. This somewhat indefinite expression is open to some criticism, but it is felt that its use will be more helpful to the reader than an attempt to discuss separately, in each case, hydrogen-ion concentration, buffer action, and base-exchange capacity.

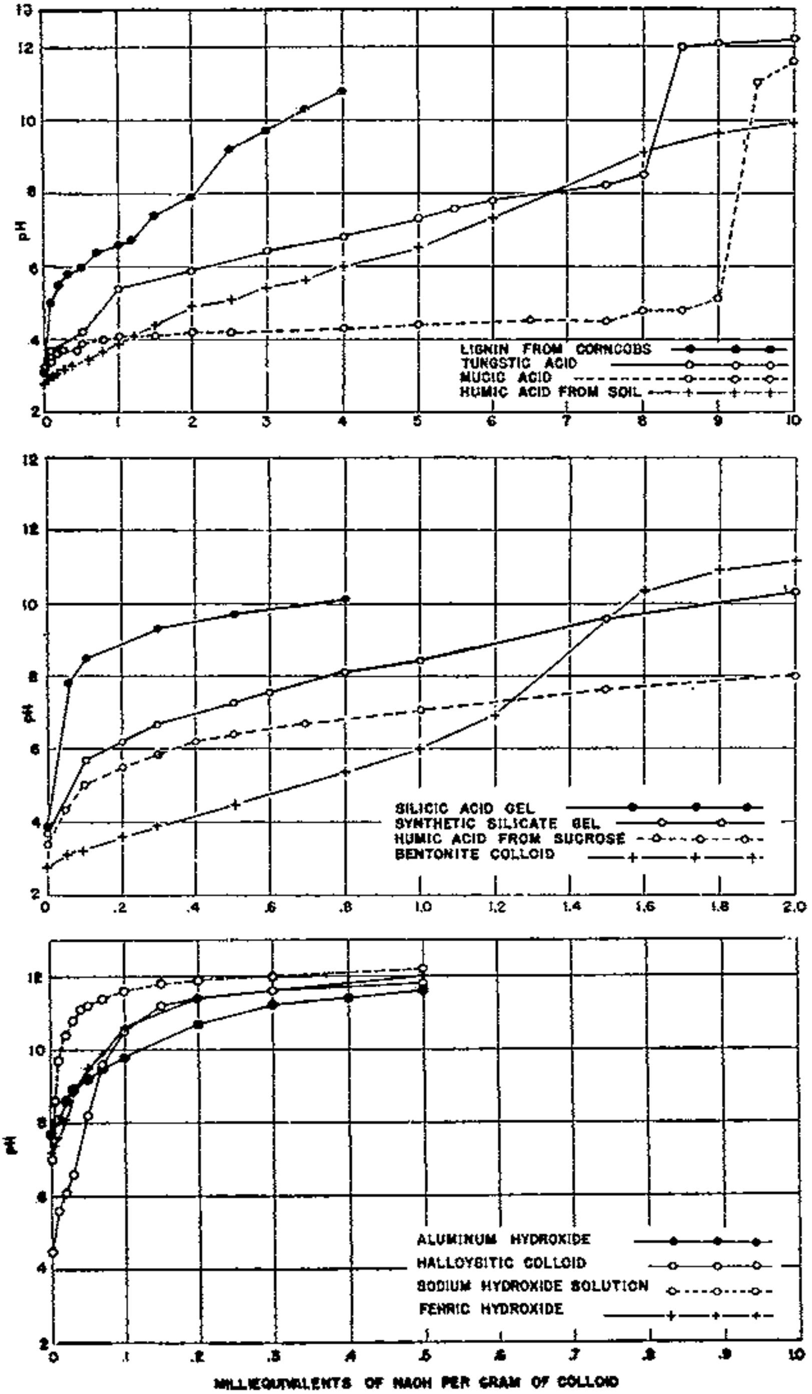


FIGURE 1.—Comparison of titration curves of various sparingly soluble acids and miscellaneous substances.

The synthetic silicate gel showed marked acidic properties. In general, however, it was less acidic than bentonite and differed considerably from bentonite in behavior with bases. Synthetic gels have previously been shown to vary in base-exchange capacity with changes in the silica-sesquioxide ratio (*40*). In this case the noncrystalline silicate gel showed acidic character similar to that of the presumably crystalline product from bentonite. Humic acid from a Podzol soil was much more acidic than either the synthetic humic acid product or the lignin preparation used. Humic acid showed acid properties comparable in some respects to mucic acid or tungstic acid, but no breaks in the titration curve were evidenced. This is in accord with the generally accepted idea that the so-called humic acid of soils consists of a group of acids rather than a single compound.

TITRATION CURVES OF SOIL-COLLOID ACIDS

Neutralization curves of the various soil colloids are assembled in figures representing in each case a complete or nearly complete profile. The graphs are divided in such a way as to facilitate translation of the laboratory determinations from them.

PEDOCAL SOILS

Titration curves for the Pima clay adobe soil profile are shown in figure 2, and those of Hastings silt loam in figure 3.

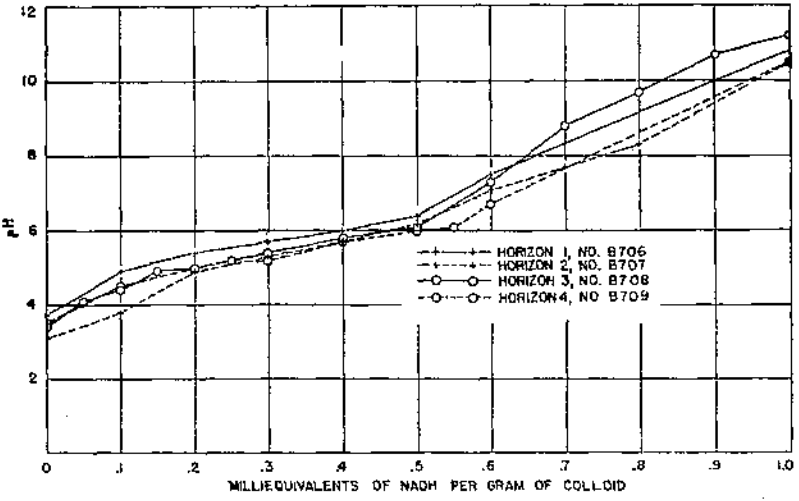


FIGURE 2.—Titration curves for colloids of a Desert soil profile, Pima series.

There is no essential difference in the character of the titration curves of the colloids of the Pima and Hastings profiles. In each case the colloids are of relatively strong acidic character. They are similar to, but distinctly weaker than, the acid of bentonite. The Pima and Hastings colloidal acids show weaker acidic character than the humic acid prepared from soil and somewhat weaker than lignin. The relatively strong acid character of the organic matter, as compared with that of inorganic soil colloid, is indicated by the fact that in the more alkaline range the curve for the untreated colloid lies in each case distinctly below the one for the corresponding material after hydrogen peroxide treatment. In each case there is some evidence of a break in the curve in the region just above pH 6, but this tendency is not very marked.

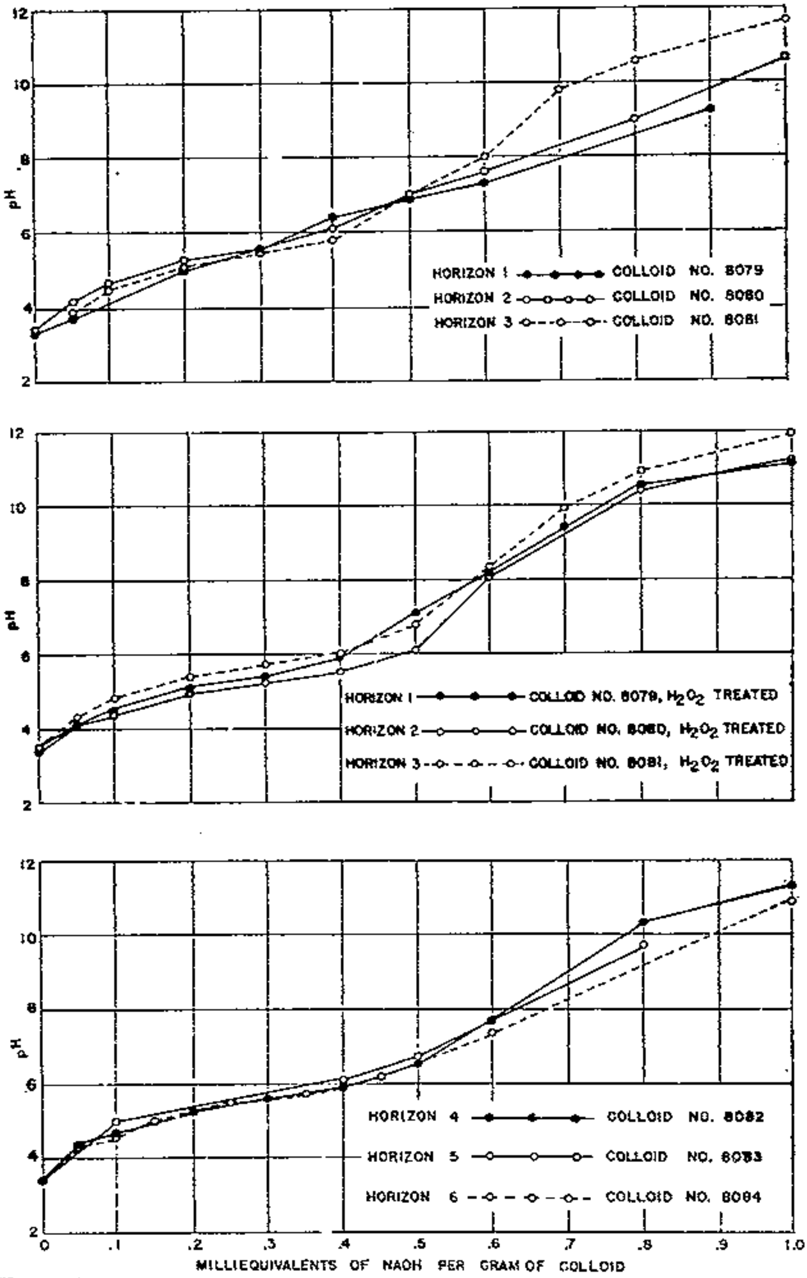


FIGURE 3.—Titration curves for colloids of a Chernozem soil profile, Hastings series.

Uniformity of material throughout the profile characterizes each of these soils. This is in harmony with the chemical compositions of most of the Pedocal soil colloids previously studied and with their general character.

PRAIRIE AND GRAY-BROWN PODZOLIC SOILS

The titration curves of the Prairie soil colloids shown in figure 4 differ but slightly from those of the Pedocals. They show a little less base-combining power, a property which is in harmony with their slightly more advanced stage of development. In the Prairie soils organic matter in the upper horizon is an important factor, and its influence upon acidic character is reflected by a very significant reduction in base-holding power when it is removed.

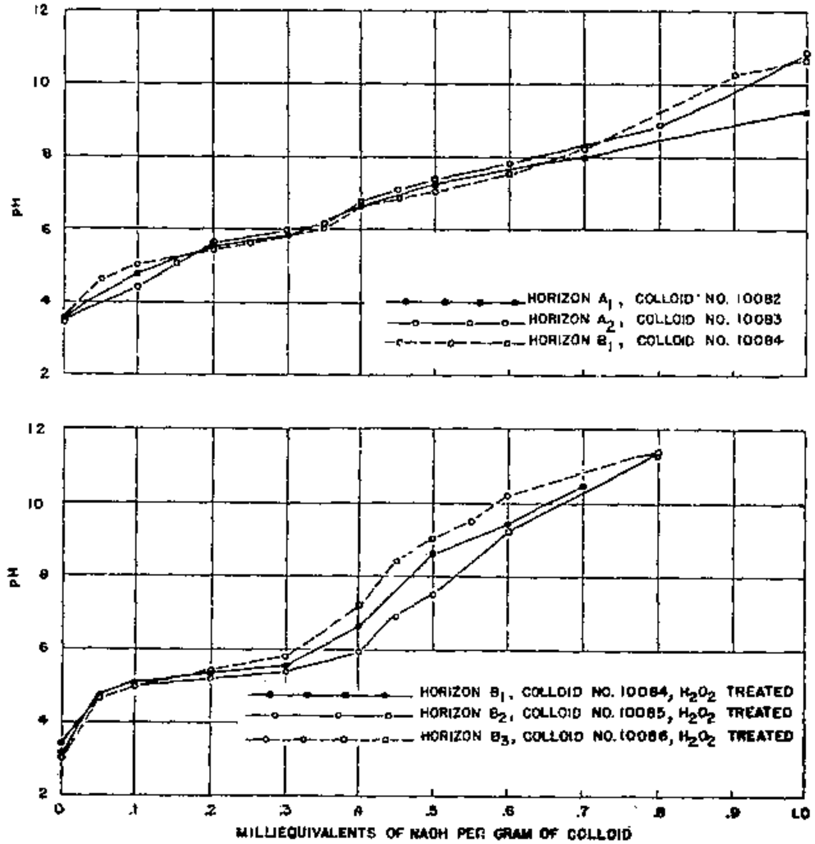


FIGURE 4.—Titration curves for colloids of a Prairie soil profile, Carrington series.

The two profiles of the Gray-Brown Podzolic group differ widely. Such a difference was expected in view of the known differences in the degree of maturity of the two profiles. The Miami profile, whose titration curve is shown in figure 5, represents a typical mature profile of this group. Its location is well to the west of the area in which this group of soils is dominant. The Miami colloids are similar in many respects to those of the Prairie group. In fact, from the standpoint of chemical composition and colloid acid behavior, they resemble the Prairies more closely than they resemble colloids of less mature profiles of the Gray-Brown Podzolic group. The Muskingum profile, whose titration curves are shown in figure 6, is representative of the less mature soils in this group.

The Miami and the Muskingum profiles present similarities as well as several sharp contrasts. In the first place, the Miami soil is derived from calcareous glacial till containing carbonate, an appreciable amount of which is present in the C horizon. The Muskingum soil is derived also from glacial till, but it is noncalcareous. Both have a relatively high feldspar content, which is indicated by the high potassium content of the colloid.

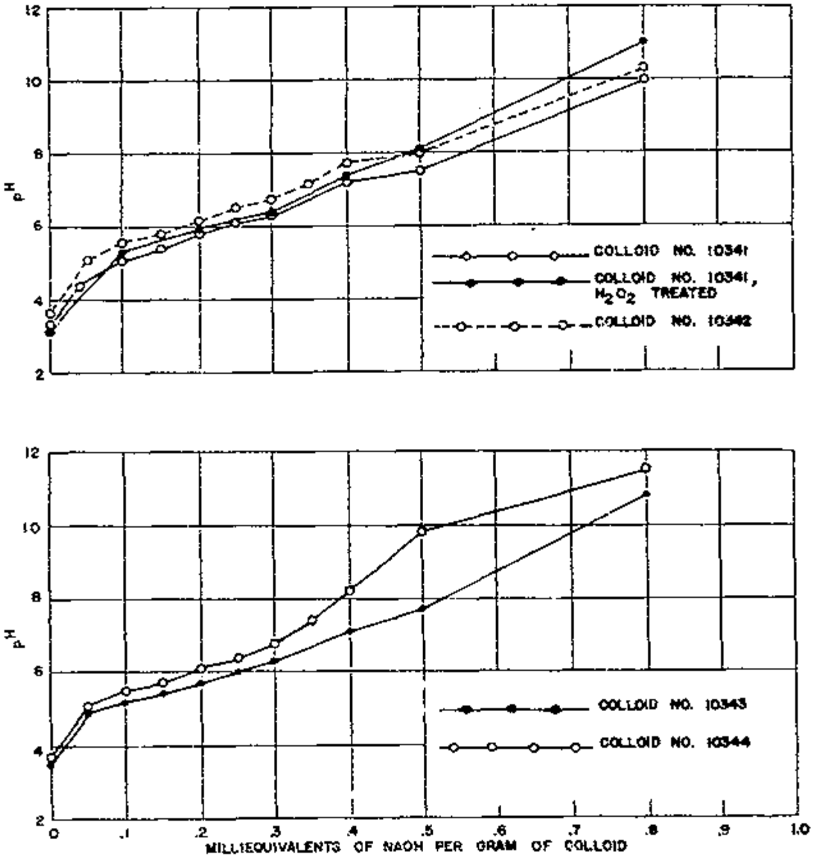


FIGURE 5.—Titration curves for colloids of a mature Gray-Brown Podzolic soil profile, Miami series.

The potash is not greatly different in the parent material of the two profiles. The soil-making processes, however, have proceeded to a markedly different degree in the two cases. The exchangeable bases of the Miami colloids bear a relationship to the total content which is similar to that frequently found in soil colloids. About 70 to 85 percent of the total calcium and a small amount of the potassium are in exchangeable form (table 5). In the Muskingum only about 20 to 40 percent of the total calcium is in exchangeable form, which is moderately less than in the Miami. The total exchangeable bases of the Miami are approximately double those of the Muskingum. This difference is reflected in the titration curves of the two soil profiles.

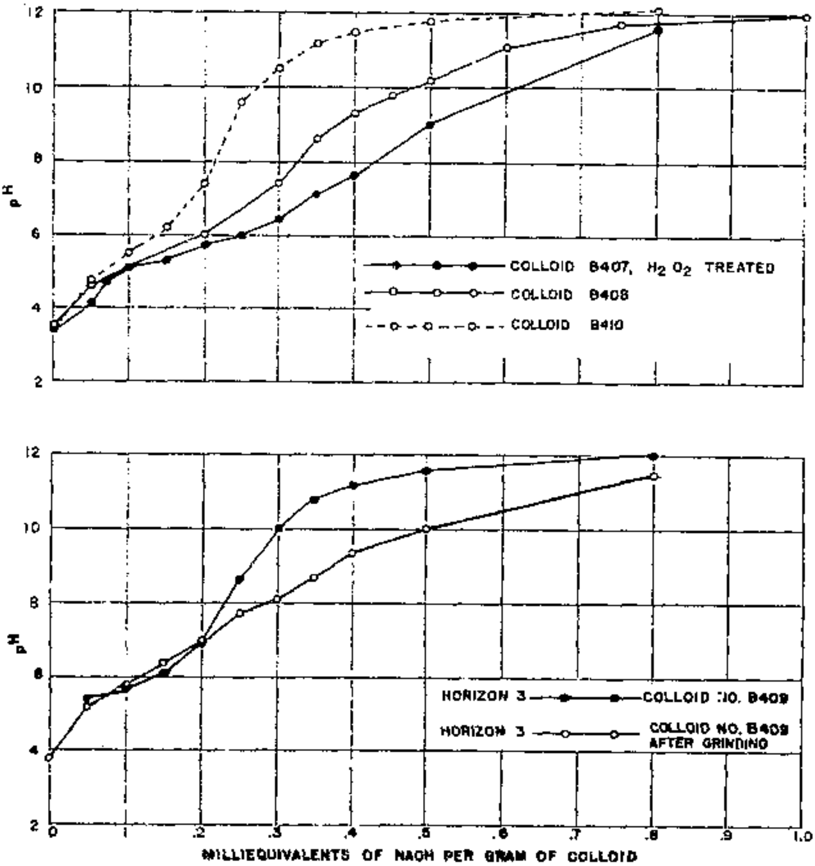


FIGURE 6.—Titration curves for colloids of an immature Gray-Brown Podzolic soil profile, Muskingum series.

A comparison of the colloids of these two profiles is of more than ordinary interest because it illustrates particularly well a relationship between total bases, exchangeable bases, and fundamental colloid character in a major soil group, which group shows considerable variation between certain soil series. It is well known from previous work that the proportion of total bases in exchangeable form varies widely for the different bases and the exchangeable portion of any particular base varies greatly in the colloids of different soils.

The major constituents of the Miami colloid differ significantly from those of the Muskingum. The silica-alumina ratio and the silica-sesquioxide ratios of the former are distinctly higher. On the other hand, the total bases of the two profiles show but little difference. The proportions of the total bases in exchangeable form are greatly different in the two profiles, and the titration curves reflect these differences, since the nonexchangeable bases are essentially inert. While not of immediate influence, the nonexchangeable bases are a source of great potential importance, not only to soil fertility but to the behavior of the colloid acids.

Proebsting (*46*) and others have called attention to the fact that a part of the nonexchangeable potassium of soils may be available to plants. The work of Kelly, Dore, and Brown (*33*) shows clearly that the nonexchangeable portion of bentonite and certain soil colloids may be rendered exchangeable by grinding in a ball mill, and also that the X-ray diffraction pattern of the colloid disappears on prolonged grinding. The possibility of changed reactivity resulting from such drastic comminution is of course marked. In order to obtain some idea of the manner in which conversion of part of the nonexchangeable bases into exchangeable form affects the apparent character of the colloid acid, a sample of electrodialyzed Muskingum colloid was ground dry in a ball mill for about 6 days, when it was again electrodialyzed. This time about 0.19 milliequivalent of titrable bases per gram of colloid was removed, which was about 50 percent of that removed by the first electrodialysis. The titration curve for the ground material is included in figure 6. It will be noted that the curves for the colloid before and after grinding are nearly identical up to about pH 7. At higher pH values, the material after grinding has much greater buffer action than before grinding. In this investigation no further attempt has been made to study the acid properties of drastically treated colloids, but this single experiment is recorded because it sets forth in a definite way the fact that the reactions of soil colloids may involve only a small part of the material included in the total analysis. However, insofar as soil-colloid behavior is concerned in the field, it appears that primarily only the reactive surface portion is of immediate importance.

The wide difference in the character of the titration curves of the Miami and the Muskingum colloids is in accord with the divergence of properties within this group shown by other methods. In the case of the B horizons, for instance, about 0.28 milliequivalent of alkali per gram was required to produce pH 7 in the Muskingum and about 0.35 milliequivalent in the Miami. At pH 10 the differences were greater. The alkali requirement of the Muskingum at this point was about 0.48 milliequivalent, while the corresponding value for Miami was about 0.75.

LATERITIC AND LATERITE SOILS

Several Laterite soils from tropical latitudes have been studied in this Division. These had very low silica contents, and in most cases the silica-alumina ratio was approximately 1 (*18*). Single horizon samples from each of these profiles were used for titration experiments. Titration curves for the lateritic Ruston profile are given in figure 7, the lateritic Nacogdoches profile in figure 8, and the Laterites in figure 9.

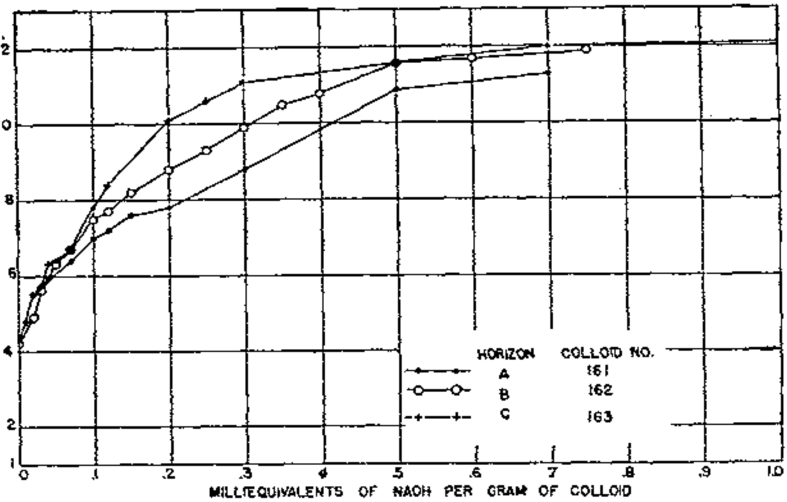


FIGURE 7.—Titration curves for colloids of a lateritic soil profile, Ruston series.

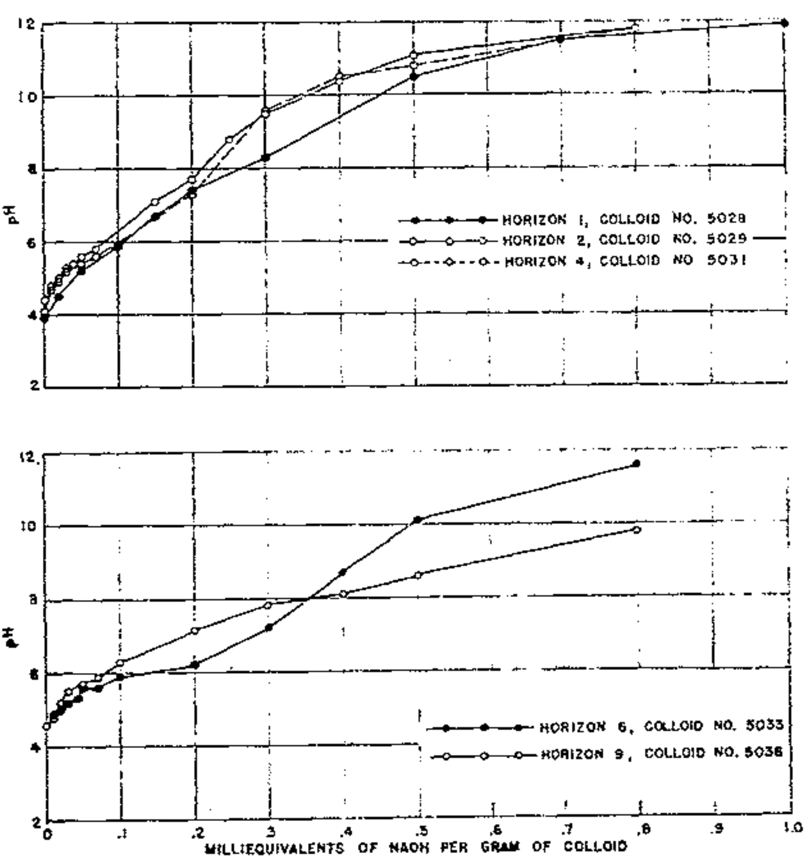


FIGURE 8.—Titration curves for colloids of a lateritic soil profile, Nacogdoches series.

The chemical compositions of the colloids of these soils reflect the extensive weathering and leaching they have undergone. In spite of their extensive weathering and leaching, however, deep horizons of the Nacogdoches profile are still markedly influenced by the character of the parent material. The silica-alumina ratio of the colloids of each horizon of the Ruston profile is very close to 2, which is that of kaolin or of partially dehydrated halloysite. It is well known that the colloids of such materials in general show very low values for such determinations as heat of wetting and the absorption of various materials. Reference to figure 1 shows the weak acid character of this class of materials. The presumption is that the Ruston colloids, freed from organic matter, give titration curves of the same general character as the one for halloysitic colloid if they are similar in constitution.

The Nacogdoches profile is also of a distinctly lateritic character. The silica-sesquioxide ratios of the two upper horizons are somewhat lower than those of the Rustons while the silica-alumina ratios are moderately higher. Several of the horizons of this deep profile were analyzed. Some of them were omitted because their appearance and chemical compositions were so closely similar. The five horizons above sample 5033 were all closely similar.

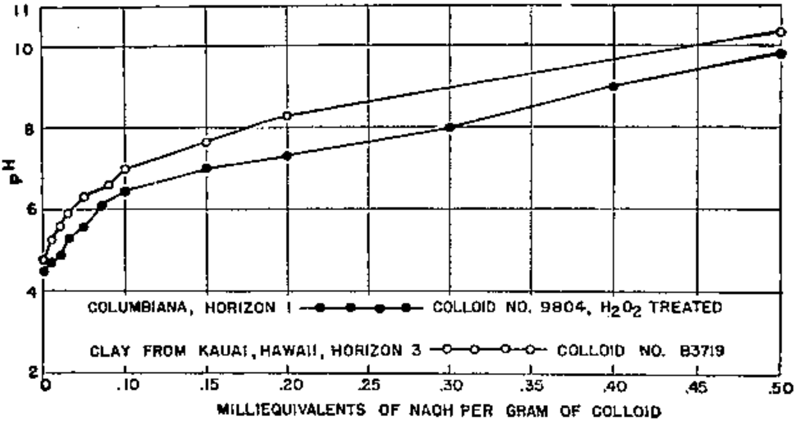


FIGURE 9.—Titration curves for colloids of single horizons of two Laterite soils.

The character of the colloid acids of the Nacogdoches profile is closely in line with what might be expected from their chemical compositions. They are weak but they are stronger than those from the Ruston soil and require a little more alkali to produce a pH value of 7.0. The general slopes of the curves of the Ruston and Nacogdoches are similar, each rising rapidly with the addition of small increments of alkali. An interesting relationship of chemical composition to behavior of colloid acid is shown by comparing horizons 4, 6, and 9. The upper horizons are representative of the soil formed in this region. Horizon 6 has a markedly different composition from that of horizon 4 or 9. In horizon 6 the silica-sesquioxide ratio is the highest of the profile, and the titration curve indicates the presence of a colloid in some respects of the most acidic character in the profile. In the colloid of horizon 9 the silica-alumina ratio is distinctly the highest of the group. The alkali requirement at pH 7 was not so high as in horizon 6, while at pH 10 the alkali requirement was much the highest of the profile. Horizon 9 is parent material consisting of calcareous greensand. Its nearly black color gives it an appearance markedly different from any of the horizons above. Greensand is generally thought to contain considerable free colloidal silica, and if such is the case with this parent material, the character of the titration curve is in harmony with its presence. It will be noted in figure 1 that the curve for silicic acid shows that very little alkali is required to produce a pH value of 7, but in the region above pH 9, the buffering effect of silica is very strong. The organic matter content of the Ruston and Nacogdoches profiles is very small and was not removed.

PODZOL SOILS

The character of colloids from Podzol soils varies widely in different horizons of a profile. In certain respects they partake of the nature of colloids of several other soil groups, and in addition present features not shared by any of the other groups. From the standpoint of the major elements of composition, represented by the silica-sesquioxide ratio, the colloids of the A_1 horizon usually approximate those of a Chernozem soil, the B horizon that of a lateritic soil, and the C horizon varies widely with the character of the parent material. Although the major elements show relationships approximating those of the colloids of other groups, it does not follow that the properties are necessarily closely similar. In the A_1 horizon of Podzols the percentage of colloid is usually very small, and the noncolloidal portion is usually very highly siliceous. Under these circumstances considerable colloidal quartz near the upper limit of particle size may be expected to be present, and its relatively inert properties may be responsible for nonconformity of colloidal behavior with gross chemical composition. In the B horizon the high sesquioxide content, presumably translocated from overlying material, is responsible for a silica-sesquioxide ratio not greatly different from those found in the Red and Yellow lateritic soils. The properties may be considerably different, however, due in considerable part to the presence of organic matter and sesquioxides presumably concentrated by fractionation in the process of transportation.

In the present study the work with Podzol profiles was less satisfactory than that with other groups for several reasons. In the first place, the colloids of the A_1 horizons usually contain but little dispersible inorganic colloid, and the small amount present is extracted only by many extractions, using large samples of soil. Then, too, it is often difficult, if not impossible, to remove the organic matter without alteration of the inorganic portion. The manganese content is frequently high enough to interfere seriously with the action of hydrogen peroxide on organic matter, or the organic matter is particularly difficult to oxidize by this reagent.

The Au Train profile was the first of the Podzols studied. It is a good Podzol, but the C horizon consists almost entirely of sand. In fact, only a slightly turbid solution could be obtained by agitation with water. It seemed not worth while to attempt a colloid extraction. The A horizons have high silica-sesquioxide ratios, and the B horizons have very low ratios. It will be noted that the organic matter content of each sample was very high; so high, in fact, that it was difficult to obtain any idea of the behavior of the inorganic portion. Titration curves for the Au Train colloids are given in figure 10. The curves for the whole colloid show it to be relatively strongly acidic. The buffering effect in the region above pH 7 is particularly strong.

Removal of organic matter from these samples was not satisfactorily accomplished with hydrogen peroxide. Data for one sample, after most of the organic matter was removed, are given in figure 10. It will be noted in the curve for the unoxidized material that pH 6.9 was reached after the addition of 1.0 milliequivalent of alkali. After oxidation only 0.4 milliequivalent was required to reach this pH value, showing that the organic portion is much more acidic than the inorganic.

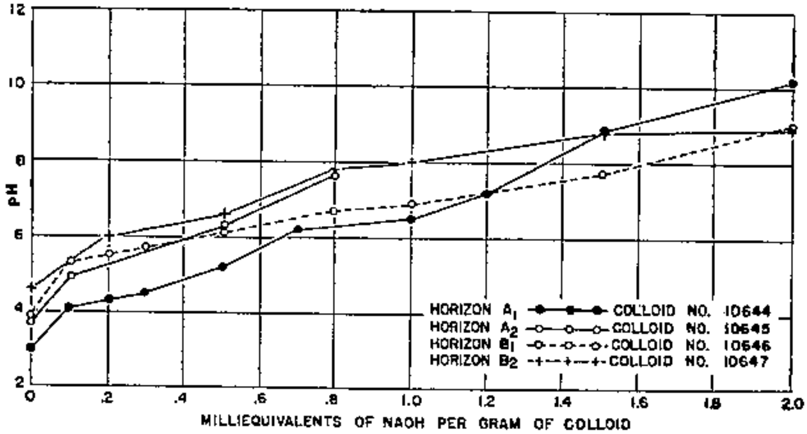


FIGURE 10.—Titration curves for colloids of a Podzol soil profile, Au Train series.

Results with the Caribou are far from satisfactory (fig. 11). The soil profile, although a well-developed Podzol, is very shallow. The four horizons extend to a depth of only about 6 inches. The quantity of soil from some of the horizons was very limited, and only small colloid samples were available. Only the colloids treated with hydrogen peroxide are included. The data are fragmentary, but are thought worthy of inclusion for comparison with the other two Podzol profiles.

The A horizon shows the highest acid qualities. This is probably due in large part to the acid quality of the inorganic colloid. Only about 16 percent of organic matter was originally present in the colloid, and this was greatly reduced by hydrogen peroxide treatments.

The colloid from the C horizon has a much higher content of potassium and magnesium than that found in the colloid of the horizon directly above it. This indicates the presence of a relatively high content of only slightly weathered minerals. The relatively weak acidic character of this colloid, as compared with the other colloids of this profile, is clearly indicated by its position in figure

11. The titration curve shows distinctly the least acidic qualities of the profile.

The Trenary profile is in some respects the best-developed Podzol of the group studied. Organic matter is very high in the surface colloid, is much less in the A_1, and again increases in the B horizon. The silica-sesquioxide ratio is high in the A_0 horizon, about the same in the A_1 horizon, and much lower in the B horizon, and in the C horizon it is considerably higher than in the B. This relationship is the one most frequently found in typical Podzols. In this, as well as the other Podzols, the calcium content is much higher in the surface horizon than in any of the others. This is no doubt due to bases taken up by the trees and left as decaying forest litter.

The organic matter of the Trenary colloids was more successfully removed with hydrogen peroxide than was that of most of the other Podzol samples studied. It was not so completely removed, however, as is usually the case with other groups of soils. An approximation of the final organic-matter content was made by deducting the percentage of original ignition loss minus the organic-matter content from the ignition loss of the treated colloid. The organic matter content of the untreated materials is given in table 3. Values for organic matter in the treated soils calculated by this means are as follows: Horizon A_0, 5.4 percent; horizon A_1, 1.1 percent; horizon B, 3.6 percent; horizon C_1, 1.4 percent. These values are of course only an approximation, but no method now in use is very satisfactory for the determination of this class of organic matter residues, the carbon content of which is not known.

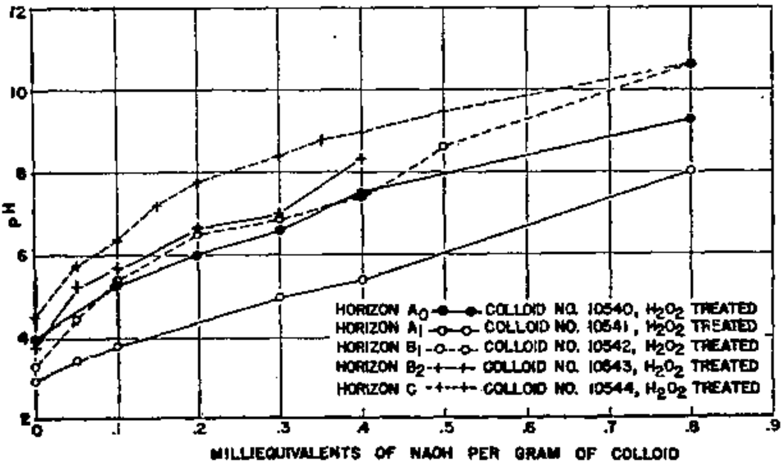


FIGURE 11.—Titration curves for colloids of a Podzol soil profile, Caribou series.

The titration curves for the Trenary colloids given in figure 12 reflect the influence of organic matter and of inorganic colloids of widely differing character. The A_0 horizon, whose colloid contains about 43 percent of organic matter, required about 1.0 milliequivalent of alkali to produce neutrality, and 2.0 milliequivalents raised the pH value to only 8.8. When the organic-matter content was reduced to about 5 percent, only about 0.35 milliequivalent of base was required to neutralize the colloid. This value is distinctly lower than the corresponding quantity for colloids of the dry-land soils, whose silica-sesquioxide ratios are somewhat lower than this one. The admixture of colloidal silica with the other portions of the colloids of the upper horizons of Podzols is again suggested.

The second horizon, A, has about the same silica-sesquioxide ratio as the A_0. The organic-matter content is much lower, and the total base content higher in spite of its strongly leached condition. The presence of but slightly weathered silicious minerals is indicated. The alkali required for neutralization was much less than that required in the A_0 horizon. Furthermore, there is but slight difference in the character of the titration curves before and after treatment with hydrogen peroxide. It is apparent here that organic acids play a minor part on account of the small amount present. However, the small percentage present is probably of relatively low equivalent weight.

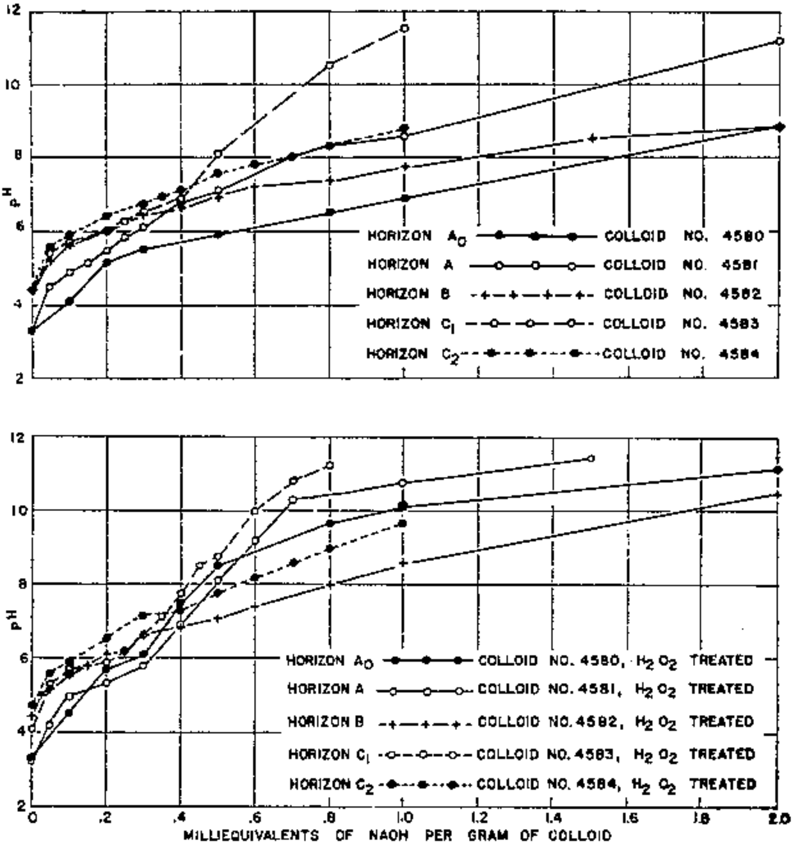


FIGURE 12.—Titration curves for colloids of a Podzol profile, Trenary series.

The B horizon presents some interesting features. The silica-sesquioxide ratio is only 1.89, as compared with 4.87 for the horizon directly above and 2.87 in the horizon beneath. It is evident that the accumulation of sesquioxide is very marked within the range of 8 to 20 inches. Accumulation of colloidal organic matter at this depth is likewise marked. The percentage is 24.22, as compared with 14.68 in the layer above and 1.87 percent in the horizon beneath.

When the organic matter was fairly effectively removed, the resulting colloid showed acid properties much more pronounced than those of other colloids of similar fundamental composition. For instance, about 0.45 milliequivalent of alkali was required to bring the colloid to pH 7. The small percentage of organic matter was of course responsible for a part of this behavior, but the colloid reacts more like one from a Prairie soil in regard to neutralization than like most of the more strongly leached samples whose silica-sesquioxide or silica-alumina ratios are of similar magnitude. There is good evidence that these colloids differ in constitution from many others of similar gross composition.

Evidence regarding the constitution was obtained through the cooperation of S. B. Hendricks of the Fertilizer Research Division of this Bureau, who made an X-ray examination of the colloids of the A, B, and C_1 horizons of the Trenary profile. Each of these horizons showed the pattern of ordovician bentonite or a mixture of montmorillonite and quartz. The A horizon showed a much more definite crystalline character than the colloids of the other two horizons. This was interpreted as indicating a greater quartz content than that of the other horizons. The pattern shown is identical with that previously found for A horizons of Podzols by Hendricks and Fry (*28*). In most other soils, however, their data show the presence of the halloysite pattern when the silica-sesquioxide ratio is below 2.

In the Trenary profile the silica-sesquioxide ratios of the C_1 and C_2 horizons are higher than the B, but the acid qualities are moderately weaker.

MAXIMUM HYDROGEN-ION CONCENTRATION

In a previous publication (*3*) attention was called to the fact that the pH values of electrodialyzed soil colloids vary with differences in the chemical composition of the colloids as well as with differences in degree of dispersion. The initial pH values shown in the various titration curves (figs. 1 to 7) do not, in most cases at least, represent the maximum hydrogen-ion concentration, or as these values are expressed, the minimum pH for the colloids. The concentrations of the suspensions used in each case were approximately the same. However, the degree of dispersion of the air-dried colloids varied widely with the chemical and physical character of the material. Also, the colloids were allowed to stand for indefinite periods while drying, thus allowing a come-back of pH to a varying degree (*2*).

In view of the fact that the colloids were all air-dried previous to use in this investigation, an attempt was made to redisperse a subsample from each of several of the colloids. Probably the most satisfactory method for dispersing the dry sample would be the same process by which they were originally separated from the soil; that is, by repeated agitation in large volumes of water, followed by centrifuging. In view of the fact that a great deal of time is required for this operation, a shorter and less satisfactory process was used. The procedure was as follows:

From 5 to 10 g of air-dry electrodialyzed colloid was added to 100 cc of water. To this was added the calculated quantity of sodium hydroxide to produce a pH value of approximately 7. The material was boiled about 1 hour, cooled, and electrodialyzed. When the electrodialysis was completed a part of the clear supernatant liquid was removed from the sample in the dialyzer. The solid was then removed with the remaining water and kneaded with a spatula, and a little of the supernatant liquid was added until a nearly homogenous material was obtained. The water content was adjusted to a point where the viscosity was near the maximum suitable for pH determinations by means of a hydrogen electrode. A pH determination was made of each sample very soon after its preparation.

Results obtained by this procedure were neither so constant nor so reproducible as are those ordinarily obtained for soil colloids. The clear, supernatant liquid was always of distinctly higher pH than the suspension of previously dried colloidal acid. As the supernatant liquid, or pure water, was added, the pH value increased. If the suspension was too viscous, the material could not be adequately stirred at the surface of the electrode. The potential readings were then unreliable.

A more or less arbitrary choice of concentration and viscosity of the sample must be made. The determination of minimum pH is seriously lacking in accuracy and reproducibility; however, such pH values are of real significance when their limitations are clearly recognized. Differences as great as 0.5 pH are thought to be highly significant. A group of minimum pH values was determined in the manner described above. These are given in table 5.

TABLE 5.—*Minimum pH values of suspensions of various electrodialyzed soil colloids*

Kind of colloid	Sample no.	Horizon	Molecular ratio $\frac{SiO_2}{Fe_2O_3+Al_2O_3}$	Minimum pH	Kind of colloid	Sample no.	Horizon	Molecular ratio $\frac{SiO_2}{Fe_2O_3+Al_2O_3}$	Minimum pH
Pima	B706	1	3.43	2.5	Trenary	4580	A_0	4.76	2.8
Do	B708	3	3.58	2.3	Do	4584	C_2	2.46	3.7
Hastings	8081	B_1	3.05	3.0	Nacogdoches	6031	4	1.26	3.5
Do	8083	B_3	3.60	2.8	Ruston	162	B	1.52	3.7
Carrington	10086	B_2	2.33	2.7	Columbiana	9804	1	.81	4.3
Muskingum[1]	B407	1	2.26	2.0	Do.[1]	9804	1	.81	3.8
Do	B409	3	1.97	2.8	Hawaiian soil	B3719	3	.44	4.8

[1] H_2O_2 treated.

The data of table 5 show clearly that there is a general relationship between the minimum pH values of soil colloids and their chemical compositions. The colloids having low silica-sesquioxide ratios give the higher pH values, and those of high silica-sesquioxide ratio give the lower pH values. The relationship, however, is far from being one of close proportionality. The contrast between the low pH values of colloids of high silica-sesquioxide ratio and the high values for those of highly lateritic ones shows very clearly that acids become progressively less acidic as hydrolysis and leaching proceed.

GENERAL RELATIONSHIPS

Neutralization curves of colloidal acids from the various soil profiles show certain similarities and certain marked differences. It is possible in several cases to distinguish the curves of one soil group from those of another, but some of the groups are too closely related to show a clear-cut distinction. Figure 13 shows the titration curves of colloids of corresponding illuviated horizons of a representative of each of the soil groups.

The factors most helpful in distinguishing similarities and differences are the following: Initial pH value of the electrodialyzed material; the alkali required to produce pH 7; and the pH range over which pH changes are most abrupt. The initial pH is of importance only in a general way, since the state of dispersion of colloid acids has an influence on pH values, as ordinarily determined. The dispersion of undried samples of colloid is fairly uniform, but air-dried material may vary widely in dispersibility. Nevertheless, when the colloids are well dispersed, the initial pH indicates the general character, since it is at its minimum in colloids of high silica-sesquioxide ratio or silica-alumina ratio and at a maximum with the highly laterized colloids. Organic colloids have initial pH values generally comparable to those of inorganic colloids whose silica-sesquioxide ratios are high. The lateritic colloids have distinctly higher pH values than the colloids of high silica-sesquioxide ratios, but such intermediate groups as the Gray-Brown Podzolics and the Podzols are highly variable.

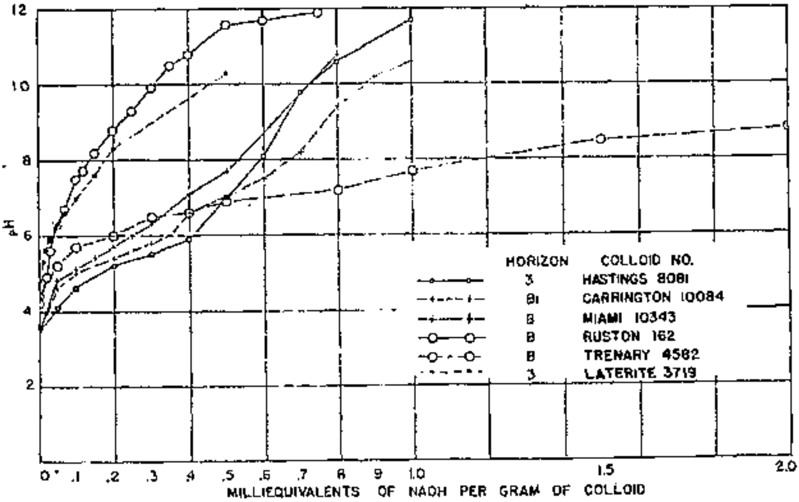


FIGURE 13.—Titration curves of colloids of corresponding illuviated horizons of a representative of each of the soil groups.

The quantity of alkali required to produce pH 7 is an expression of base-exchange capacity and is perhaps the best single criterion by which to judge the character of the colloidal acid. The Pedocal soil colloids require about 0.55 milliequivalent per gram to reach the neutral point, those from the Prairie soils just a little less, approximately 0.5, and the Gray-Brown Podzolic group covers the range from nearly 0.5 to about 0.2, which is near the maximum quantity required by the lateritic colloid. The typical Podzols are highly variable, and no particular alkali requirement can be said to be characteristic of the colloids of their profiles or even of corresponding horizons of different profiles. The character of the inorganic colloid is variable throughout the profile and widely different in different profiles. The same general relationship between horizons is found, however, in that the B horizon has the lowest alkali requirement.

In working with soil-colloidal acids, it is important to keep in mind that not all the material is involved in the reactions given. The nonexchangeable base content is a highly variable part of the whole of the bases. The exchangeable portion is as low as 5 percent of the total in some cases; in other cases more than 60 percent. Practically the whole of the nonexchangeable bases remains inert throughout electrodialysis and subsequent neutralization. If the colloids were ground in a ball mill or otherwise drastically treated, in most cases the base requirement for neutralization would probably be significantly increased. Colloids thus treated would then not be characteristic of the soils from which they came, but would reflect the influence of this greatly accelerated weathering action.

The type of curve over the whole range of alkali additions is the most characteristic feature which distinguishes profiles from one another. Some groups are best characterized by the behavior in one pH range, and other groups of colloids in another pH range.

Curves for colloids of high silica-sesquioxide ratio differ fundamentally from those for colloids of low ratio. Those of high silica-sesquioxide ratio rise slowly in pH with additions of alkali until a point around neutrality, that is, between pH 6 and 8, is reached. As more alkali is added, the pH rise is more rapid, suggesting the neutralization of a definite but weak acid at a point around pH 7. The curve shows only the characteristics of a monobasic acid, but this does not preclude the possibility of polybasicity with neutralization characteristics comparable to those of tungstic acid (p. 14).

Colloidal acids of low silica-sesquioxide ratio, such as those of the Ruston soil series, behave very differently from those of the dry-land soils. The rise here is rapid on addition of alkali. There is a general deflection in the curve in a region around pH 8, but there is no break sharp enough to give much evidence of the neutralization of a single definite acid.

The curves shown by the untreated Podzol colloids give no evidence of the presence of a single definite acid. The material is perhaps a mixture of weak and relatively strong acids. Their most characteristic feature is that of strong buffering in the alkaline region. The alkali-soluble humic acid extracted from one of the Podzols showed no marked break on titration, but had acid characteristics more marked than those of any of the inorganic soil colloids (*56*). Such organic colloid is so strongly buffered in the alkaline range that addition of 10 milliequivalents of alkali per gram does not raise the pH value above 10.

Several investigators have found marked breaks in the titration curves of soil or soil colloids in the region around pH 7. The work of Denison (*25*) emphasizes this characteristic. Such behavior is sometimes interpreted as indicating the presence of a sparingly soluble true acid of monobasic character. The results obtained by different workers vary widely, however. This variation is probably due in part to differences in the kinds of materials used, and in part to their condition and to technique of neutralization. Mukherjee and

Sen (*42*) found a single marked break, most pronounced in the region between pH 6 and 8. Bradfield and Cowan (*12*) found some evidence of two dissociation constants, while Puri (*47*) gives evidence that the acidoid of clay in a fully saturated condition behaves like a tribasic acid.

There is no conclusive evidence from the data regarding the basicity of the various colloids. Of the soil-colloid acids studied here, it seems highly probable that some at least may be polybasic in structure and monobasic in behavior. In some cases the titration curves show a distinct break between certain pH values. In other cases such evidence is almost, if not entirely, lacking. Such breaks as occur show wide differences in degree of abruptness and are not all found within the same pH range.

No one type of curve and perhaps no one compound can be said to be characteristic of soil colloids. They cover the range of variation from the curve shown by a very weak acid, such as that of the colloid of halloysite material, or Laterites, to the type characteristic of the much stronger clay acid, bentonite.

Comparison of the total exchangeable bases given in table 4 with the base-exchange capacity at different pH levels shown on the various graphs brings out several facts.

In the Pedocal soil colloids the exchangeable bases are in each case higher than the base-exchange capacity for sodium made at pH 7. This is due in part to the fact that in their natural state the pH values were above 7 and in part to the fact that in many instances a somewhat smaller amount of sodium is required to attain a particular pH than is the case with calcium or magnesium. The colloids whose natural condition is acid of course require more equivalents of alkali to produce pH 7 than are found in the sum of the exchangeable bases. The surface horizon of a Miami profile is normally somewhat acid, but the particular sample used had a pH value of 7. This fact together with its relatively high organic-matter content and natural calcium saturation readily accounts for the fact that 0.49 milliequivalent of exchangeable bases per gram was found by analysis and only 0.38 milliequivalent of sodium hydroxide was required to produce pH 7.

Further attention should be given to the usefulness of titration curves as a means of detecting similarities and differences in soil colloids. Perhaps no criteria thus far utilized are more satisfactory as a means for comparing the acid character of soil colloids than are titration data over a wide range of hydrogen-ion concentration. Some colloids may be similar at one pH and widely different in another range. Some colloids may be changed by certain treatments and others not appreciably altered. When titration data are plotted side by side, the significance of the variations is in most cases more far reaching than are conventional determinations, such as ammonia-absorbing power or base-exchange capacity at a single pH value, which are widely used.

CHARACTER OF COMPOUNDS PRESENT

The data presented in this bulletin add a little to the vast accumulation of information upon which hypothesis have been based regarding the character of the individual acid or acids responsible for the acidic behavior of soil colloids. It is not proposed to offer here any new hypothesis regarding the chemical constitution of the colloids, but it does seem appropriate to call attention to the way in which some of the recently proposed theories are in accord with or stand in opposition to the present data.

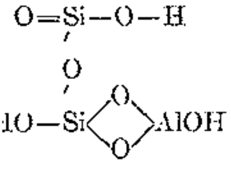
Wadsworth (*60*) in a recent paper concludes from an examination of the various available data that the soil colloids are probably mere mixtures of the oxides of silicon, aluminum, and iron. This view appears to be much less widely held, however, than was the case a few years ago. From the standpoint of neutralization data there is strong evidence that the major constituents are not present entirely as a simple mixture of oxides. No one of the three constituents taken alone even approximates in acid character the colloids of the dry-land soils. It is true that the hydrogen-ion concentration of silicic acid may be as high as any of the soil colloids, or higher, but base-holding power and buffer action through the region of moderate alkalinity is so much less as to indicate that most of the soil-colloid acids are vastly stronger acids, or, at least, have much greater base-neutralizing capacity than the most acid of the individual major inorganic constituents.

The thesis of Truog and coworkers (*22*, *34*, *59*), namely, that one definite compound is responsible for the property of base exchange, is neither strongly supported nor entirely denied by the present data. The base-holding property increases with increase in the acidic constituent (silica) out of proportion to the increase in the quantity of this constituent. This suggests that a stronger acid occurs when more silica is present rather than a greater quantity of a weaker acid. To be specific, colloids with silica-alumina ratios of 4:1 usually have lower pH values than do those whose ratios are 2:1, and they neutralize more than twice as much base. It is possible, however, that smaller particle size and the consequent reaction of a greater proportion of the entire mass may be responsible, in part at least, for these disproportionate values.

Perhaps it should again be emphasized that there is some evidence that a smaller proportion of the total mass of the particles probably takes place in the reaction when the silica-alumina ratio is low than when it is high (table 4). Furthermore, if we recognize the X-ray and optical evidence presented by Hendricks and Fry (*28*), Kelley and coworkers (*33*), Bray (*13*), and others, there is strong indication of the presence of a major compound in colloids of high silica-alumina ratio different from those in colloids where this ratio is low. Terminology varies, but the differences are significant.

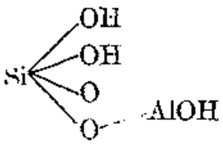
The general features of the hypothetical constitution of colloids presented by Byers (*17*), by Brown and Byers (*14*), and by Byers, Alexander, and Holmes (*18*), are, for the most part at least, compatible with the present data. Some of the significant features follow.

Bentonite colloid and the colloids of the dry-land soils represent the nearest approach to the montmorillonitic acid type of colloid included in these studies. The silica-alumina ratio in several cases is distinctly above 4, but it is far below the theoretical value of 6, sometimes postulated for the montmorillonitic colloid (*37*, *48*). The presumption is, therefore, that little if any of the material with a ratio of 6 is present, but that material with a ratio of 4 may be admixed with a little quartz or amorphous silica. It has been suggested also that the correspondence of the X-ray pattern of the montmorillonite with that of colloids whose ratio is about 4 may be due to the fact that crystalline structure persists after a considerable alteration of composition takes place. The ratio of approximately 4 suggests the presence of the material called pyrophyllic acid by Byers (*17*), with the formula



This formula represents an acid which is tribasic and presumably of relatively strongly acidic characteristics. These features are well in accord with its neutralization curve, although its curve gives no evidence of more than dibasic character and very little evidence of more than one replaceable hydrogen atom.

The next hypothetical step postulated is that of halloysitic acid, with the following formula



This material, with its weaker acidic qualities, is well in accord with the titration behavior of the extensively weathered colloids whose silica-alumina ratios are around 2. Those having ratio values lying between 2 and 4 may well be presumed to be mixtures of the hypothetical acids, halloysitic and pyrophyllic, although oxides and perhaps other compounds may be present. On the basis of the nomenclature adopted by Bray (*13*) from the work of Larsen and Wherry (*37*), materials intermediate between these two groups, and having a silica-sesquioxide ratio of 3, are known as the beidellite-nontronite type of clay material. These are found in the Prairie and Gray-Brown Podzolic groups.

CHARACTER OF COLLOID ACID AND SOIL FERTILITY

No definite data are available regarding the crop-producing power of the various soils included in these studies. The general character of their fertility is well known, however, from soil-survey reports and from extensive field observations. From this information certain generalizations may be made. With the exception of the group of true Podzols, the general level of fertility parallels the base-exchange capacity of the colloid at neutrality, that is, the alkali required to produce pH 7. When this value for the colloid is more than about 0.45 milliequivalent per gram, the crop-producing power is apt to be limited by water supply more than by lack of chemical constituents. Fertility decreases as reduction in this factor reflects more extensive hydrolysis and leaching, and finally, when a value below 0.2 is reached, one expects to find it necessary to resort to feeding of plants by the addition of complete fertilizers at frequent intervals, if profitable crops are to be grown continuously. Other features of the titration curve, such as the degree of buffering at the higher pH values, also bear a relationship to fertility. The Podzol colloids, with their very high content of acid organic matter, are not easily compared with colloids which are essentially inorganic.

The titration curves for the colloids of soils of widely varying character indicate the manner in which lime-requirement determinations made by different methods might be expected to vary, depending upon the pH attained in the procedure.

In some cases, such as those of the various horizons of the Ruston series, the change in pH on the addition of small increments of alkali is so marked around the point of neutrality that it makes but little difference whether the method assumes pH 6.5 or 7.5 as the objective. On the other hand, in a highly organic soil, such as the A_0 horizons of the Trenary series, base-exchange capacity varies widely with the pH value at which approximate base equilibrium is attained. The magnitude of the base requirement for pH 7 in highly organic soil materials is in accord with the well-known fact that the lime requirements indicated for certain acid organic soils are so high as to be prohibitive from the practical agricultural standpoint.

SUMMARY

The acids of colloids extracted from the profiles of various major soil groups were studied.

The chemical composition of the colloids of various soil profiles are given, together with their exchangeable bases.

The pH values of electrodialyzed colloids vary with the chemical composition of the colloids. Those with high silica-sesquioxide ratios tend to have lower pH values (2.5 to 3.0), while the pH range of colloids of low ratio is usually from 3.5 to 4.5.

The character of neutralization curves made with sodium hydroxide varies widely for colloids of the different soil groups. The colloids of Pedocal soils show the strongest acid character. About 0.55 milliequivalent of sodium hydroxide per gram of colloid is required to produce a pH value of 7. There is considerable evidence of a break in the curve for these colloids between pH 6 and 8.

To facilitate interpretation of the data, titration curves for several sparingly soluble materials not of soil origin are given. These materials include tungstic acid, mucic acid, ferric hydroxide, aluminum hydroxide, silicic acid, and other compounds.

The colloids of the lateritic soils have much weaker acid qualities than those of the Chernozem soils, and their titration curves are of such markedly different form that the two groups are readily differentiated by this means. The Prairie group and the Gray-Brown Podzolic group have titration curves intermediate in character between those of the Pedocal and the lateritic soils.

The curves for the colloids of true Podzols are widely different for adjacent horizons of a particular profile, and corresponding horizons of different profiles show wide variation in acidic qualities as well as in chemical composition.

The acid character of the colloidal organic matter is in most cases so pronounced that when such organic matter is present in considerable quantity it tends to obscure the behavior of the inorganic portion.

The acid qualities of the bentonite colloids are distinctly stronger than those of the inorganic soil colloids but weaker than humic acid extracted from the soil.

The acid character, brought out by titration data, is related in a general way to the fertility of a soil.

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